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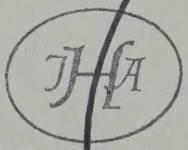

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THE PROPERTIES OF SILICA

AN INTRODUCTION TO THE PROPERTIES OF SUBSTANCES IN THE SOLID NON-CONDUCTING STATE

BY

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American Chemical Society
Monograph Series

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Science

GENERAL INTRODUCTION

American Chemical Society Series of Scientific and Technologic Monographs

By arrangement with the Interallied Conference of Pure and Applied Chemistry, which met in London and Brussels in July, 1919, the American Chemical Society was to undertake the production and publication of Scientific and Technologic Monographs on chemical subjects. At the same time it was agreed that the National Research Council, in coöperation with the American Chemical Society and the American Physical Society, should undertake the production and publication of Critical Tables of Chemical and Physical Constants. The American Chemical Society and the National Research Council mutually agreed to care for these two fields of chemical development. The American Chemical Society named as Trustees, to make the necessary arrangements for the publication of the monographs, Charles L. Parsons, Secretary of the American Chemical Society, Washington, D. C.; John E. Teeple, Treasurer of the American Chemical Society, New York City; and Professor Gellert Alleman of Swarthmore College. The Trustees have arranged for the publication of the American Chemical Society series of (a) Scientific and (b) Technologic Monographs by the Chemical Catalog Company of New York City.

The Council, acting through the Committee on National Policy of the American Chemical Society, appointed the editors, named at the close of this introduction, to have charge of securing authors, and of considering critically the manuscripts prepared. The editors of each series will endeavor to select topics which are of current interest and authors who are recognized as authorities in their respective fields. The list of monographs thus far secured appears in the publisher's own announcement elsewhere in this volume.

The development of knowledge in all branches of science, and especially in chemistry, has been so rapid during the last fifty years and the fields covered by this development have been so varied that it is difficult for any individual to keep in touch with the progress in branches of science outside his own specialty. In spite of the facilities for the examination of the literature given by Chemical Abstracts and such compendia as Beilstein's Handbuch der Organischen Chemie, Richter's Lexikon, Ostwald's Lehrbuch der Allgemeinen Chemie, Abegg's and Gmelin-Kraut's Handbuch der Anorganischen Chemie and the English and French Dictionaries of Chemistry, it often takes a great deal of time to coördinate the knowledge available upon a single topic. Consequently when men who have spent years in the study of important subjects are willing to coördinate their knowledge and present it in concise, readable form, they perform a service of the highest value to their fellow chemists.

It was with a clear recognition of the usefulness of reviews of this character that a Committee of the American Chemical Society recommended the publication of the two series of monographs under the auspices of the Society.

Two rather distinct purposes are to be served by these monographs. The first purpose, whose fulfilment will probably render to chemists in general the most important service, is to present the knowledge available upon the chosen topic in a readable form, intelligible to those whose activities may be along a wholly different line. Many chemists fail to realize how closely their investigations may be connected with other work which on the surface appears far afield from their own. These monographs will enable such men to form closer contact with the work of chemists in other lines of research. The second purpose is to promote research in the branch of science covered by the monograph, by furnishing a well digested survey of the progress already made in that field and by pointing out directions in which investigation needs to be extended. To facilitate the attainment of this purpose, it is intended to include extended references to the literature, which will enable anyone interested to follow up the subject in more detail. If the literature is so voluminous that a complete bibliography is impracticable, a critical selection will be made of those papers which are most important.

The publication of these books marks a distinct departure in the policy of the American Chemical Society inasmuch as it is a serious attempt to found an American chemical literature without primary regard to commercial considerations. The success of the venture will depend in large part upon the measure of coöperation which can be secured in the preparation of books dealing adequately with topics of general interest; it is earnestly hoped, therefore, that every member of the various organizations in the chemical and allied industries will recognize the importance of the enterprise and take sufficient interest to justify it.

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PREFACE

The experimental work of the past two decades has yielded a large amount of information on the chemical and physical properties of silica and the silicates, but much of it has remained rather inconveniently scattered through the scientific and technical periodicals. To bring this information together in a convenient and accessible form is an obviously useful service, and some work in this direction which I had already begun received encouragement in the form of an invitation from the Editor of these Monographs to prepare a book on "The properties of silica and the silicates."

The compilation of the material was not very difficult, but what did it all mean? During those same two decades our knowledge of the structure of matter and the properties of energy had progressed tremendously. The desirability of relating the collected facts to the new general principles, and of giving the whole assemblage a more thorough and fundamental treatment than had first been planned, became more and more evident as the work advanced. The result has been a delay of several years beyond the date originally set, with a book on pure silica only to show for the labor.

The recognized function of a preface is to give the history of the work, but I shall venture to enlarge that function by indicating what is my ideal for such a book.

Often, while trying to extract a meaning from a lot of apparently unrelated facts resulting from my own experiments or obtained by other workers on silica and the silicates, have I wished that I could turn freely to some individual who combined in one brain all of Bohr's and Rutherford's insight into the structure of the atoms, Gibbs' and Planck's comprehension of the relations between energy and the forms of matter, Maxwell's and Drude's penetration into the principles of electric and radiant energy, together with the detailed knowledge of silica possessed by Dana, Des Cloizeaux, Rose, and a host of others. I have dreamed of inducing this super-scientist to write for me a book which should show how all the many qualities which we define and measure and call "properties" are interrelated, and how each is related to the constitution and structure of silica and the silicates, all this to be in language such that any of us of average intelligence and experience,—whether student, researcher, ceramic engineer, or petrologist,—would be able to understand the facts and principles and apply them to his daily problems.

One of the outstanding characteristics of this ideal book would be its

brevity. The properties of matter as exemplified in silica would appea as a homogeneous whole, not parceled out into chapters, each the exclusiv province of a certain group of specialists.

An even more important characteristic of the ideal treatise would b that the second edition, incorporating all the results of the latest research would be shorter than the first edition. This shrinkage in size woul follow logically from the principle that science is organized knowledge,— the more knowledge, the better organization.

Such a book would be a delight to the type of scientist whom Planck calls the "purist." For him, the laws of nature are now fully revealed at least in their broader outlines, and it only remains to fill in the picture with more accurate details. But there is a second kind of information to be considered, It consists of scattered and ill-formed bits of knowledge for which even our imaginary super-scientist has been unable to find a place in his current scheme of things. They are the raw material of laws and principles as yet undiscovered, and for that very reason are unclassifiable. A place must be found for them in our ideal book; the best guess possible must be made as to what part of the periphery of science they belong in, and enough description of them must be given so that they shall not be forgotten.

With a solid core of classified fact and principle, and a decorative fringe of significant but unclassifiable residues, our ideal physico-chemical treatise on silica is now complete.

I shall not dwell on the painful contrast between the foregoing dream and the reality. Within the limits set by ignorance and the pressure of other duties, I have endeavored to produce a book on the properties of silica which should be on a plan sufficiently logical to serve either as an outline for the properties of any similar substance, or as a framework for the insertion of the record of future advances in our knowledge of silica. The book has thus tended to take the form of a text-book on the properties of substances in the crystalline and glassy states, with silica as the leading example. Perhaps it will not be without some usefulness in this direction, although not to be compared in thoroughness, of course with any of the standard reference works. I can see large gaps in it which might easily be filled by additional work on material now available and other parts which could be considerably improved with the aid of a little experimental work. Some of these deficiencies may be corrected in a future edition.

In accordance with the general plan outlined above, the material has tended to group itself under the following outline:

A general introductory chapter on the properties of substances is followed by a series of chapters on particular properties. Under the general plan, each chapter should contain:

(1) The briefest possible statement of the meaning of the property under consideration. It is hoped that this will save the reader some of the labor of searching through the library for information about an unfamiliar property and prevent his being misled by the different constants, units, or technical terms used by different authors. But these paragraphs must necessarily be brief, and, if the reader be wholly unacquainted with the subject, will have to be followed up in the standard text-books and periodicals of physics and chemistry, to which references will have been given.

(2) A summarized statement of our present knowledge of the property as applied to silica. This for the benefit of the reader who wants concise information in a hurry, unencumbered with any confusing exceptions or qualifications.

(3) In a few instances, a discussion of the degree of constancy of the so-called "constants" for the forms of silica.

(4) A review of the experimental work upon which the more general statements are based. I have consulted the original published record in nearly every case and have sometimes supplemented this by correspondence with the author about doubtful points, or by consultation with others better acquainted than I with the subject-matter. I have computed all the new tables and prepared all the illustrations (excepting the lettering) and hope that the errors have thus been kept within reasonable limits.

(5) Hypotheses. One of the important needs of research on silicates is a good supply of fruitful hypotheses—hypotheses not of an irresponsible, *a priori* kind, but of the kind from which predictions can be made, to be tested experimentally. During the past fifty years the theory of the silicates has been too dependent upon the analogies of organic chemistry, and until very recently sufficient use has not been made of the principles developed by investigators in the field of physical chemistry. Furthermore, the benefits should be reciprocal, for in the long step forward which is now being taken in our knowledge of molecular and atomic structure, investigators should be able to draw very considerable aid from the immense body of facts already assembled by mineralogists and other students of silicate chemistry. I have therefore not hesitated to introduce hypotheses wherever they seemed useful in summarizing the facts or in indicating the way to further knowledge; being careful to keep clear the distinction between what is well-founded and what is purely speculative, at the same time recognizing that no so-called "fact" can be completely free from hypothesis, and no hypothesis which an investigator is willing to entertain can be wholly unrepresentative of facts.

The rule of brevity, mentioned in the description of the ideal book on silica, applies up to this point. Genuine additions to our knowledge ought to make it possible to shorten rather than expand the material

outlined above. Those who have done experimental research can best realize how large an amount of time and labor is required to secure by experiment a small amount of really new information, and they can also appreciate that the results of months or years of research, if it is research of the highest grade, can often be condensed into a very few pages of tables or curves, while the really significant exceptions can be made to stand out in their proper perspective.

There remains still a third type of material for the book, to which the rule of brevity cannot be made to apply so strictly. This material includes: (1) historical notes; (2) information on the appearances of silica in nature, and its relations to the descriptive and historical sciences; and (3) information concerning the industrial uses of silica. These subjects can be extended ad libitum, a temptation I have tried to resist.

The chapters on natural occurrence and industrial sources and uses are considerably condensed, because good reference books are available which this book need not try to replace. On the mineralogy of silica Dana's *System of Mineralogy* and Hintze's *Handbuch der Mineralogie* remain the standards for reference, while many books are available on the different branches of ceramics and industrial chemistry into which silica enters as raw material or finished product.

In closing this Preface, I wish to acknowledge gratefully my indebtedness to the large number of individuals who have aided in the preparation of the book by their counsel, criticism, or information, particularly my colleagues the Director and members of the staff of the Geophysical Laboratory of the Carnegie Institution of Washington, and my friends in the Bureau of Standards and elsewhere. I should like to mention particularly the following, who have read and criticized one or more of the chapters: Messrs. L. H. Adams, E. T. Allen, F. J. Bates, N. L. Bowen, W. G. Cady, W. W. Coblentz, A. L. Day, C. N. Fenner, P. D. Foote, P. R. Heyl, P. Hidnert, W. J. Humphreys, R. D. Mailey, G. E. Merritt, H. E. Merwin, G. W. Morey, C. G. Peters, E. Posnjak, H. S. Roberts, E. S. Shepherd, F. B. Silsbee, W. Souder, W. F. G. Swann, R. C. Tolman, L. B. Tuckerman, E. W. Washburn, H. S. Washington, E. T. Wherry, W. P. White, F. E. Wright, R. W. G. Wyckoff, and E. G. Zies. At the same time I must absolve any and all of those mentioned from responsibility for errors such may easily have been overlooked, or they may have been inserted by the author after the chapter was read. I shall appreciate the favor if any reader who notes errors and omissions will call attention to them either in published reviews or by private correspondence.

ROBERT B. SOSMAN.

November, 1926.

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THE PROPERTIES OF SILICA

Part 1. Fundamentals

Chapter I. THE PROPERTIES OF A SUBSTANCE

The substance silica

Our knowledge of the external or natural world is mostly a knowledge *objects*. The almost infinite variety in the combinations of properties hibited by natural objects can be reduced to the understandable order science with the aid of the hypothesis that objects are built up of *bstances* in limited number, each substance having definite and repro-ıcible properties.

The effort of physical and chemical science has been to make this ımber as small as possible. Three stages are to be distinguished in the cent history of this effort:

(A) The recognition of about 90 *chemical elements*, from which all substances are compounded according to definite laws.

(B) The discovery of radioactivity and of the existence of *isotopes*, which seemed for a time to reverse the desired direction of evolution by increasing the number of elements.

(C) Discoveries made during the last two decades, which appear to be leading toward a reduction of the number of independent elements to 2, namely, the positive electron and the negative electron.

Silica, whose properties form the subject-matter of this book, has long en recognized as a substance. It consists, as recognized in stage (A), the two chemical elements: silicon and oxygen.

Facts developed in stage (B) show further that it consists of 3 kinds silicon and 1 kind of oxygen.

We are still in the midst of stage (C), but are already in possession a considerable amount of knowledge concerning the constitution of e four kinds of elementary chemical substances which make up the bstance silica.

The line between fact and hypothesis will be drawn in this book be-ween stages (B) and (C) and silica will be treated as a substance con-sting of the two chemical elements silicon and oxygen. The facts and ypotheses regarding its composition and atomic structure will be con-dered more fully in the second and third chapters.

The measurable physical properties of a substance

Working with the substances defined by the chemist, the physicist attempts to describe the infinite variety of natural phenomena in terms of certain fundamental *physical laws*. To some of these laws all substances respond alike. For example, at a given place on the Earth's surface the rate of fall of any mass of a substance in a vacuum, at the end of one second, is the same whatever the substance. Such laws are outside and above the range of such a book as this one, whose purpose is to expound the behavior of one particular substance, not of matter in general.

There are other laws,—more limited in scope simply because our knowledge is more limited,—to which the response of all substances is not the same, and the behavior of each substance must then be characterized by certain so-called *properties of the substance*. These properties may be of every degree of generality, depending upon the generality of the laws in which they apply.

Like the chemist's effort to reduce to the minimum the number of his elements, is the physicist's attempt to make the number of physical properties as small as possible; but being by nature more inclined to philosophy he tries, while he is about it, to include the whole of physico-chemical science, and to state it all in terms of a still more limited number of *fundamental concepts*.

It is easy to see, however, what it is that both are striving after. Both chemist and physicist are searching for something analogous to what the mathematician calls *invariants*, not necessarily the things that are indestructible, but the things whose trail can be followed unbroken through a whole series of physico-chemical changes, actual or imagined.

The fundamental concepts

A certain amount of choice is allowable among the important concepts of physico-chemical science respecting the question which shall be called "fundamental," because there are well-recognized interrelations among them. Hence a concept taken as fundamental in one set of quantities may, in another set, be given rank as secondary or derived. Nevertheless, there is general agreement that the number of fundamentals can not conveniently be reduced below 5 unless we are willing to undertake deep-seated modifications of our current views. It is necessary to recognize at least 5 things which can not be defined so as to be dependent upon anything more fundamental.[1]

For convenience of exposition, we shall increase the number to 6 and

[1] Tolman, R. C., *The measurable quantities of physics*, Phys. Rev. (1917) (2) **9**: 237-253. Interrelations undoubtedly exist which could be used to reduce the number both of physical and of chemical fundamentals, but they must be classed for our present purposes as "theoretical." See, for example, Lunn, A. C., *Atomic constants and dimensional invariants*, Phys. Rev. (1922) (2) **20**: 1-14.

e the following quantities, all of which are additive (extensive) in
aracter:

1. Length (L)
2. Time interval (Z)
3. Mass (M)
4. Electric charge (E)
5. Entropy (S)
6. Energy (U)

The first three of these quantities are the basal concepts of the gen-
al doctrine of *mechanics*. With the fourth added they constitute the
undation of *electrodynamics*. The addition of the fifth quantity com-
etes the necessary fundamentals of *thermodynamics* in its most general
ise. The sixth is the concept which ties together all the phenomena of
ysics and chemistry, the concept of an indefinable but indestructible
nething whose total quantity does not change but whose manifestations
ange from one point of place or time to another.[2]

No discussion is necessary of the first four of our six fundamental
antities, but the fifth may chance to be less familiar to some of the
amic and petrologic readers of this book than to the chemists and
ysicists, and so may deserve an additional word here. The concept
entropy is nothing more than the quantitative statement of the daily
servation of science that our universe appears to be going hell-bent
vard some distant and invisible dead level. Increase in entropy is the
antitative measure of its downward progress. Seen from another point
view, it expresses the fact that the configurations which have the
gher mathematical probability are the more likely to occur in nature.[3]

When entropy is taken as fundamental, *temperature* is a derived quan-
y, defined in terms of energy and entropy by the formula: $T = \mathrm{d}Q/\mathrm{d}S$
ere $\mathrm{d}S$ is the infinitesimal change in entropy corresponding to the
sorption of the heat energy $\mathrm{d}Q$ in a reversible process. This is the
undation of the absolute thermodynamic, or Kelvinian, scale of tem-
rature,[4] on which the melting point of ice is 273.10°K. This scale will
used frequently in later parts of this book, especially the theoretical
rts, and will be designated by the abbreviation "K."

[2] Perhaps what we actually do is first to observe a natural law, then find what
ntity in it is conserved in such a way that we feel justified in calling that quantity
ergy"; but this is a philosophical question which we cannot here enter into. See
ANN, W. F. G., Science (1925) **61**: p. 427.

[3] For the original definition of entropy, the concept which underlies the Second
w of Thermodynamics, see CLAUSIUS, R.: Ann. Phys. u. Chem. (Poggendorff)
65) **125**, p. 390. Best recent discussion: LEWIS, G. N., & RANDALL, M., *Thermo-
namics and the free energy of chemical substances* (1923, New York) pp. 109-154.

[4] For the original definition see THOMSON, W. [Lord KELVIN], Trans. Roy. Soc.
inburgh (1854) **21**: p. 125. For a comparison of the scientific temperature scales:
CKINGHAM, E., Bull. Bur. Standards (1907) **3**: 237-293. For a review of the
sent status of temperature scales, theoretical and experimental: DAY, A. L., &
SMAN, R. B., *Realisation of absolute scale of temperature*, in GLAZEBROOK's *Dic-
nary of applied physics* (1922, London) I, 836-871.

Combinations of the fundamental concepts

The number of combinations of 6 things, taken 2, 3, 4, 5, or 6 at time, is 57. Accordingly there are 57 possible groups of physical law which state relations between the 6 fundamental concepts which we hav adopted, and some of these laws require the statement of characterist properties for any substance to which they may be applied. Our ide complete work on the properties of a substance might then be logical divided into not more than 57 chapters, according to the number and kir of fundamental concepts under consideration.

Of course the existing system of physico-chemical science has n developed in any such formal way as is indicated in the foregoing par graphs. New concepts in great number have sprung up from time time, and have then spread and coalesced with others, like the spreadir crystallites growing from many centers in a glaze or in a glassy lav Nor have they all coalesced yet, by any means. It remains true, thoug that the physical character of each of them as related to other more fund mental concepts,—not necessarily the 5 or 6 listed above,—is expressib in the form of a product of powers of the quantities which are taken fundamental, and this expression is called the *dimensional formula* the new quantity.[5] In the completed ideal work, then, we must imagi each of our chapters to be subdivided according to the different ways which its quantities can be combined to give dimensions to new secon ary quantities.

A still further subdivision of different character is now necessar namely, one based upon the atomic constitution of our substance.

The atomic constitution of matter

The most fundamental fact about silica is that it consists of atom which themselves contain electrons.

The philosophical or the practical reader may protest that this is n fact, but theory,—and that fact and theory should be kept clearly di tinct. In reply, he may be asked to define the difference between fa and theory. Certainly our present evidence for the existence of aton and electrons is much more varied and complete than is our evidence f the existence of the Moon, yet no one seriously considers the Moon be merely a working hypothesis, useful only for classifying and teachi some of the facts of astronomy. An author desiring to write a boo about the Moon might base his phenomenological discussion entirely certain visual sensations which recur about every twenty-eight days, reser ing for the final chapter the hypothesis that there really is a spheric object revolving about the Earth and reflecting the light of the Sun, b would not his work be much simpler if he were to start by taking th hypothesis as a fact?

[5] See Bridgman, P. W., *Dimensional analysis* (1922, New Haven).

The truth is that no supposed scientific "fact" is completely free from ypothesis. For example, it might seem that the statement that "the ensity of quartz at 20°C is 2.6495" is a statement of fact, but it is not, ecause it involves the hypothesis that quartz is everywhere the same ubstance, an hypothesis which is inherently improbable and is still nproved, as will be shown at a later page. Even the statement that "a ertain piece of quartz picked up near the Geophysical Laboratory in July, 923, has a density at 20°C of 2.6495" is not a statement of fact, for it nvolves the hypothesis that the density of this fragment has not changed ince it was measured; this may not be true, because having been but ecently uncovered by building operations this fragment may be exhibit- ng an elastic lag and may still be expanding slightly from the relief of ie pressure under which it formerly stood.

Thus every statement of fact in this book must be viewed as trailing vith hypotheses, expressed or implied, which it is the task of science to nake off as rapidly as possible by trial and experiment, but which will ever be completely removed from the so-called facts to which they dhere.

Practical classification of the properties of silica

Even though the atomic constitution of silica be taken as an admitted act, it remains true that the atoms are so small that they are not directly erceptible to any human sense. The objects with which we usually deal onsist of many millions of atoms, and in many respects the behavior of uch a swarm is different from that of a single atom or small atom-group.

Between the two extremes,—atom and tangible object,—lies a range f dimensions often claimed as the province of colloid chemistry. This nvolves forms of silica which I shall refer to in this book as "micro- hases," and also silica in atomically thin fibers and sheets, particularly t bounding surfaces between phases. Our task, then, is to find the pplication of our logically possible combinations of fundamental physical uantities to the following 3 states:

(1) silica in bulk
(2) micro-phases of silica and bounding surfaces of silica
(3) atomic and molecular silica

It is not a logical classification, but it is forced upon us by the fact nat our eyes and our fingers are perfectly enormous objects, real uni- erses; while our perceptions are so slow as to seem like the dragging of eologic time, when compared with the motion of an atom.

This further classification does not necessarily multiply the number f subdivisions of the subject by 3, since the concept of entropy has no pplication to single atoms or to assemblages containing such small umbers of atoms that the properties of the assemblage are not a definite nean of the properties of the individuals regarded as a completely dis-

ordered swarm. All combinations in which entropy enters are therefore without present application to atomic and molecular silica.

Next, as to the starting-point. Most of our experimental information is obtained under the conditions under which we ordinarily live, namely, a pressure of about 1 megabarye and a temperature of 15 to 25°C, usually referred to as "room temperature". From this starting-point we work out toward higher pressures and toward both higher and lower temperatures. The limits are set only by experimental practicability, for the absolute zero of temperature is just as inaccessibly distant as the maximum temperature [6] of matter, as would be at once obvious if we used a logarithmic scale of temperature.

A systematic and complete application of the foregoing outline is not now practicable, but it will at least furnish a guide toward a classification of the huge bulk of data that is available. The following paragraphs give an outline of this kind as applied to silica. The chapters of this book will follow this outline with certain changes of order made desirable by the character of the material.[7]

Outline of the properties of silica as treated in this book

The chemist's task comes first. Having discovered a substance called *silica,* which can be caused to disappear by various means, then to reappear with its original properties, he proceeds to dissect it into its more elementary constituent substances *silicon* and *oxygen,* distinguishing also between three kinds of silicon which he finds in it. (Chapter II.)

Going still deeper into its mass composition he examines the constitution of the atoms and the little that is known about the mode in which they combine to form the substance silica. (Chapter III.)

His knowledge of atoms and their modes of arrangement and combination being too scanty to permit of further logical progress in this direction, he starts on a new tack, and collects all the different kinds of pure silica that can be found or made. Some of them, it turns out, differ in properties from others, and behave differently when heated or stressed. They are the *polymorphous forms* and *states of aggregation* of silica. The complete description of their relationships as affected by temperature and pressure can be embodied in a *phase-rule diagram* (Chapters IV, VI, VII, VIII), and their *rates of transformation* may be studied empirically at the same time. (Chapters V, VII.) The practical necessity of treat-

[6] See Mellor, J. W., *The zenith temperature,* Trans. English Ceram. Soc. (1924) **23**: 13.

[7] Only a few references have been given in this chapter, but the reader may be assured that it contains nothing essentially new. It may seem an impractical beginning to a highly practical subject, but before being launched upon so complex a task as the orderly description of all the properties of silica, the reader may have welcomed a general discussion whose purpose is to show the demands, as well as the limitations, of the task. This chapter deserves more care than all the rest of the book put together, and I regret that it has not been better done.

ng the micro-phases separately is also recognized. (Chapters IX, X, and XI.)

One obvious consequence of the atomic constitution of silica is the existence of differences in *symmetry* and in certain characteristic *dimensions* between the polymorphous forms. (Chapters XII and XIII.) To round out the picture, *hypotheses* of structure and polymorphism must now be brought in. (Chapters XIV to XVII.)

The chemist is now ready to examine and record the fundamental properties of his collection of polymorphous forms, those properties which will enable him to predict completely the behavior of silica under any conceivable circumstances. He recognizes at once a relation between the fundamentals M and L, namely, that the ratio of M and L^3 is a quantity characteristic of each form of the substance,—its *density* or *specific volume.* (Chapter XVIII.)

By this time the physicist has had to be called in to explain what controls the appearance and disappearance of the forms discovered in the earlier chapters. The cause sought for proves to be a relation between the fundamentals U and S,—energy and entropy,—most conveniently stated in the form of a property called the *zeta,* whose study requires the measurement of the *heat capacities* and *latent heats* of the forms. (Chapter XIX.)

This important relation of U and S, which expresses the *availability* of energy as it is made available through matter (M), is seen to be paralleled by two other relations: that between U and L, which leads to the idea of a *storage* of energy within a definitely limited space; and that between U, Z, and L, which leads to the idea of a *transmission* of energy from point to point during an interval of time.

The introduction, into each of these combinations, of other fundamental concepts of the set of six then leads further to the idea of *kinds of energy* which are mutually convertible, namely: M, to mechanical energy; E, to electromagnetic energy, in the most general sense of the word; and S, to thermal energy, the kind which flows in only one direction.

Electromagnetic energy in the general sense, furthermore, we may separate for practical purposes of discussion into the three kinds: (1) energy of the electric field, (2) energy of the magnetic field, and (3) energy of the periodic electromagnetic field, the last covering the very important kind known usually as radiant energy, including light and the X-rays.

Mechanical energy is further distinguishable into: (1) gravitational energy, with which we shall not be concerned since we are dealing only with silica in small masses and at the Earth's surface; (2) kinetic energy, with which likewise we shall not be directly concerned because its laws are believed to be general for all substances and not dependent on specific properties; (3) volume energy; (4) surface energy; and (5) energy of shape.

Finally, we introduce the concept of the *transformation of energy,* in its association with matter, from one of these forms into another. Many of these transformations must be stated in terms of specific properties of the substance involved.[8]

A crude classification of the properties of a substance such as silica, in their relation to the storage, flow, and transformation of energy-forms as discussed in the preceding paragraphs, is shown in Table I. The numerals indicate in a general way the chapters in which the property in question is described.

Chemical properties

The reader whose training has been in chemistry or ceramics rather than in physics will perhaps be disappointed in not having found in this or in succeeding chapters any reference to the "chemical properties of silica". But it will be seen easily that from the point of view adopted for this presentation there is no such thing as a chemical property of an individual substance, unless we wish to include under that term the conditions of equilibrium and the rates of transformation of its polymorphous forms. Chemistry is concerned with the interactions between two or more substances, and chemical properties may only be spoken of, consequently, in connection with a system of two or more components. The solubility of silica in water, for example, is not a property of silica, but an item in the general plan of the two-component system SiO_2:H_2O.

Chemical properties as usually described in the text-books are of three general kinds: (1), indications as to the number and kind of phases produced when the substance under discussion is mixed with other substances to form a poly-component system; (2), physical properties of such a poly-component system; and (3), data on the rates of reaction in the poly-component system, often under rather ill-defined conditions. Information of these three kinds would evidently be out of place in the present book, and may properly be left to a volume in which poly-component silicate systems can be considered.

[8] Mention should also be made here of the transformation of matter *into* energy (the inertia of energy), but, like gravitational energy, this is a subject with which we shall not be concerned in dealing with silica under terrestrial conditions.

TABLE I. CLASSIFICATION OF THE PROPERTIES OF SILICA, IN THEIR RELATION TO THE STORAGE, FLOW, AND TRANSFORMATION OF ENERGY.

	Chemical energy	Thermal energy	Mechanical energy				Electromagnetic energy		
			Kinetic energy	Volume energy	Energy of shape	Surface energy	Electric field	Magnetic field	Periodic electromagnetic field
STORAGE OF ENERGY....	Latent heat Zeta XIX	Heat capacity XIX	Specific volume XVIII	Compressibility XXII	Rigidity XXIII	Surface tension XXV	Dielectric constant XXVI	Magnetic permeability XXIX	
TRANSMISSION OF ENERGY	Rate of inversion V	Thermal conductivity XXI					Electric conductivity XXVII		Refraction XXX XXXI XXXII
									Rotation XXXIII
									Reflection XXXV
Effect of temperature		Temp. coefficient of thermal cond. XXI					Temp. coeff. of elec. cond. XXVII		Temp. coefficients of refraction etc. XXXIV
Effect of pressure and stress									Stress-birefringence XXXIX
Effect of electric and magnetic fields.....									Electro-optic and magneto-optic constants XL
CONVERSION OF ENERGY into: Thermal energy ..			Flow (fluidity, viscosity) Plastic flow XXIV				Resistivity Dielectric anomalies XXVII		Absorption XXXVI
Mechanical energy. Volume energy..		Thermal dilatation XX	Failure (gliding, cleavage, fracture) XXIV				Electrostriction XXVIII	Magnetostriction	
Shape energy ..		Thermoelasticity							
Energy of electric field		Pyroelectricity XXVIII Thermoelectric power		Piezo-electricity XXVIII					
Energy of magnetic field		Pyromagnetism		Piezo-magnetism					
Energy of periodic electromagnetic field	Flame luminescence XXXVIII Phosphorescence	Emissivity XXXVI	Tribo-luminescence XXXVII						Fluorescence Scattering XXXVIII

Chapter II. THE COMPOSITION OF SILICA

The elementary composition of silica

To the best of our present knowledge the substance silica is a true chemical compound. Its composition is constant, being represented by the following proportions of its elements by weight:

Silicon	46.72 per cent
Oxygen	53.28 per cent

Character of the evidence

The characteristic feature of a chemical compound is that its elementary composition remains the same, even though it be prepared from different sources, or be put through manipulations which cause it temporarily to disappear. Accompanying this constancy of composition, in most cases, is a corresponding constancy of physical properties.

It is hard for silica to qualify under these criteria. Silica is such a stable substance that its analysis into its chemical elements is a difficult task. Accordingly our belief that it is a true compound does not rest upon chemical analysis. Nor does it rest upon chemical synthesis, for elemental silicon is hard to prepare pure. As for constancy of properties, silica prepared in different ways exhibits a wide variety of properties. We assemble and correlate these variations by the assumption that silica can exist in different *polymorphous forms*. This assumption has proved satisfactory. (See p. 48.)

In spite of this scarcity of direct experimental proof, we shall accept, as everyone now does, the statement that silica is a true chemical compound which fits in with our general system of chemical compounds in accordance with the law of simple proportions.

On the basis of this assumption, the elementary composition of silica can be calculated from the combining weights of silicon and oxygen, as determined with the aid of various other compounds of silicon and of oxygen.

Yet even on this basis there remains an uncertainty as to the true proportions of silicon and oxygen in silica, an uncertainty which may be conservatively estimated at one-third of one per cent. This may seem absurdly large in these days of exact and careful atomic weight determinations, especially in view of the fact that among all the substances found in nature crystalline quartz is one of the purest. Yet there are good grounds for the estimate, grounds of two widely different kinds.

One is the uncertainty in the atomic weight of silicon due to the experimental difficulties in its determination. The other lies in the fact that the element silicon is a mixture of *isotopes*.

Uncertainty in the atomic weight of silicon

Within the memory of every reader of this paragraph (at least in this year of its publication), the internationally accepted atomic weight of silicon has been lowered from 28.4 to 28.06, a change of a little over one per cent. The present accepted value, 28.06, depends mainly upon the determinations by Baxter, Weatherill, & Scripture [1] on $SiCl_4$ and $SiBr_4$. Their mean result differs from the average of previous determinations by 0.19 or about two-thirds of one per cent (28.06 as compared with 28.25). Thus our estimate of an uncertainty of at least one-third of one per cent is not over-conservative. Furthermore, are we sure that some of the earlier determinations were not just as correct as the latest one? In other words, is there more than one kind of silica on the Earth's surface?

Isotopes

For the past one hundred years chemists have speculated on the reason why so many elements have atomic weights which are very nearly whole numbers.

The suspicion that all the elements have been built out of some primordial element of atomic weight = 1, and that more exact data would prove that all atomic weights are whole numbers, was repeatedly negatived by experimental determinations on elements such as silver and chlorine, whose combining weights could be measured with great exactness, and whose atomic weights nevertheless departed from whole numbers by much more than the possible error of measurement. The next obvious suspicion, that the elements whose atomic weights are not whole numbers are really mixtures of two or more elements of identical chemical properties, was too improbable to be seriously considered, and was furthermore likewise repeatedly negatived by the agreement between atomic weight determinations on material obtained from very different sources. Chemists had therefore become accustomed to the fixed belief that the atomic weight of an element is really an invariable constant of nature. So when the investigations of Boltwood, Marckwald, Welsbach, Soddy, Hahn, and others had shown that certain radioactive elements are indistinguishable chemically and even spectroscopically, and yet have different atomic weights, the chemists hesitated to believe that such a thing could be possible in any but the new and unfamiliar radioactive group.

The clue to the mystery had already been furnished by Soddy in the development of the theory of radioactivity. It was found that a radioactive element could lose one alpha particle, of atomic weight 4, and two electrons of negligible atomic weight, and still retain its chemical properties unchanged. The two elements thus differing in atomic weight

[1] Baxter, G. P.; Weatherill, P. F.; & Scripture, E. W., Jr., Proc. Amer. Acad. Arts & Sci. (1923) **58**: 245-268.

but indistinguishable chemically were called *isotopes*. Soddy thus had a good basis for the suggestion that "Chemical homogeneity is no longer a guarantee that any supposed element is not a mixture of several of different atomic weights, or that any atomic weight is not merely a mean number".

The next step was to hunt for isotopes among the non-radioactive elements. J. J. Thomson, by his so-called "positive ray" experiments, showed that neon might perhaps consist of two elements of atomic masses 20 and 22, mixed in such proportion as to give the mean atomic weight 20.2 which is found by density measurements on the pure gas. Aston, successfully developing the analysis of positive rays with his "mass-spectograph", and Harkins, Brönsted, and others experimenting with various methods of separation of isotopes, proved conclusively that not only neon, but also chlorine and various other elements with fractional atomic weights are really mixtures of isotopes.

Isotopes in silicon

Among these mixed elements is silicon. It consists for the most part of silicon of atomic mass 28, whose symbol may be written Si^{28}. Mixed with the Si^{28} are small amounts of heavier kinds of silicon of atomic masses 29 and 30 (symbols Si^{29} and Si^{30}).

The above-mentioned facts immediately raise the important question: Is chemical "silicon", wherever it is found, always a mixture of these three silicons in the same proportions? If not, then the atomic weight of silicon from different parts of the Earth's surface will vary with the locality from which it comes.

Oxygen, on the other hand, as far as has yet been determined, is homogeneous and consists everywhere of only one kind of atom. Hence if the proportion among the silicon isotopes is not a constant, the weight-percentages of silicon and oxygen in silica may vary with the locality, even though it be a strictly pure chemical substance of the formula SiO_2.

The experimental evidence now available indicates that the isotopous elements on the Earth's surface, as well as in meteorites, contain their isotopes in constant proportions; in other words, the atomic weights are in fact natural terrestrial constants, though they may not be natural cosmic constants. An exception must be made, of course, for elements such as lead (Pb) which have been and are now being produced by radioactive decomposition. Another possible exception, not due to the cause just referred to, is boron.

Silicon is among those isotopous elements whose atomic weight appears to be a terrestrial-meteoritic constant. If it is, then the percentage composition of silica, by weight, is likewise a constant, and its properties will be found to be the same everywhere on the Earth.

On the other hand, the possibility of differentiation of elements on the

Earth needs to be kept in mind. From this point of view the evidence is not as full as could be desired, and the isotope question will continue to be present in the background as a disturbing suspicion whenever discrepancies in the quantitative constants of silica can not be explained as due to experimental error or chemical impurities.

Experimental evidence on the proportion of isotopes in silicon

The existence of silicon isotopes was discovered by Aston. The best quantitative evidence is by Jaeger & Dijkstra.

The silicon fluoride examined by Aston[2] contained at least two kinds of silicon, one of atomic weight 28, the other of atomic weight 29. There was also a suggestion of a small quantity of a third silicon of atomic weight 30, but the evidence was not conclusive.

Subsequent investigations by Mulliken and by Aston have proved definitely the existence of Si^{30} in addition to Si^{28} and Si^{29}. Evidence of all three is found by Mulliken[3] in the band spectrum of the nitride SiN. Isotopes Si^{29} and Si^{30} are definitely shown by Aston[4] in experiments on zirconium fluoride.

The only direct evidence on the proportion of the isotopes in silicon has been furnished by Jaeger & Dijkstra.[5] They compared the densities of specimens of tetra-ethyl-silicane, $Si(C_2H_5)_4$, made from silica from 6 terrestrial sources and from 6 siliceous meteorites (chondrites). The silica was first separated by the usual fusion with sodium carbonate and treatment with hydrochloric acid, and was then converted into silicon tetrafluoride by way of ammonium and barium fluosilicates. The tetrafluoride, finally, was transformed into tetra-ethyl-silicane by reaction with magnesium ethyl bromide in ether. The compound is a colorless liquid boiling at 154.95°. It was purified by repeated reaction and by fractional distillation. The density was determined with a precision of 0.0004 per cent by means of a pyknometer. The results are shown in Table II.1.

The differences in density from the mean are not over 0.006 per cent, but are real, because this is more than ten times the precision of measurement. The question is on the interpretation of the differences.

The atomic volume of the isotopes of an element is constant, hence the density of the mixed element or of any of its compounds will vary with the proportion among the isotopes in the element. If the differences found in the present case were due to such a cause, the differences in atomic weight would be as shown in the fourth column of the Table. They are evidently so small, if real, as to be beyond the reach of atomic weight determinations by chemical means.

They can be further examined, moreover, by a study of the refractive indices. The refractive index, like the atomic volume, is independent of the

[2] Aston, F. W., Phil. Mag. (1920) (6) **40**: 628-634, pl. 14. *Isotopes* (1922, London) p. 74.

[3] Mulliken, R. S., Phys. Rev. (1925) (2) **26**: 319-338.

[4] Aston, F. W., Phil. Mag. (1925) (6) **49**: 1191-1201, especially p. 1198.

[5] Dijkstra, D. W., *Over de mengverhouding der isotopen van het silicium*, Proefschr., Groningen, 1924. Jaeger, F. M., & Dijkstra, D. W., Kon. Akad. Wet. Amsterdam, Proc. Sect. Sci. (1924) **27**: 393-406.

atomic mass, but differs in character from the atomic volume in that it can be measured directly without reference to a measurement of weight. The differences in index, which can be measured differentially with high precision, are shown in the fifth column of the Table. They are seen to change oppositely to the densities instead of remaining at zero, and therefore indicate strongly that the small differences of density are due to minute amounts of impurities which could not be removed by distillation.

The atomic weight of the silicon of these 12 specimens is therefore constant within 0.03 per cent.

TABLE II. 1.

SPECIFIC GRAVITY OF TETRA-ETHYL-SILICANE MADE FROM SILICA FROM VARIOUS SOURCES (JAEGER & DIJKSTRA).

Mineral source	Geographic source	Sp. grav.* at 19.935° C	Corresponding variation in at. wt.	Variation in refr. index $\times 10^6$
	TERRESTRIAL SILICA			
Quartz sand	Groningen, Netherlands	0.76730	— 0.0095	+ 26
Quartz sand	Germany	0.76732	— 0.0057	+ 24
Quartz sand	Pennsylvania	0.76730	— 0.0089	+ 82
Analcite	Seiser Alp, Tirol	0.76740	+ 0.0095	— 5
Leucite	Tavolato, near Rome, Italy	0.76738	+ 0.0057	— 2
Chlorite	Pfitschtal, Switzerland	0.76736	+ 0.0019	+ 5
	METEORITIC SILICA			
	Alfianello, Italy (16 Feb. 1883)	0.76735	— 0.0006	+ 18
Peridotite-enstatite-chondrite	Soko-Banja, Serbia (13 Oct. 1877)	0.76735	+ 0.0006	+ 12
Enstatite-chondrite	Holbrook, Arizona (19 Jul. 1912)	0.76735	+ 0.0006	+ 13
Hypersthene-olivine chondrite	Ochansk, Perm, Russia (30 Aug. 1887)	0.76738	+ 0.0057	Reference
	Bjurböle, Nyland, Finland (12 Mar. 1899)	0.76735	Reference	+ 2
	Kesen, Rikuzen, Japan (12 June 1850)	0.76735	+ 0.0006	+ 1

* Referred to water at the same temperature, in a vacuum. (F. M. JAEGER, correspondence with the author.)

POSSIBILITIES OF DIFFERENTIATION

What possibility is there of finding any evidence of differentiation? The three silicon isotopes have the same chemical properties, so no chemical process will separate them. But they do differ considerably in atomic mass, hence thermal or gravitational gradients might be effective. In any undisturbed portion of molten magma the heavier molecular units, say the $Si^{30}O_2$, might concentrate toward the bottom, leaving an excess of $Si^{28}O_2$ near the top. This would at least be consistent with the fact that our mean atomic weight for silicon is nearer 28 than 29, and suggests that we look for silicon of highest atomic weight in the rocks which have come from the greatest depth.

With respect to this point Jaeger & Dijkstra's selection of specimens is not completely satisfactory. Their terrestrial silica is all continental silica from the northern hemisphere. The three specimens of quartz sand are probably products of the disintegration of continental granitic rocks, which we now suppose to be a resultant of radial differentiation within the Earth. The other three specimens are all from the land mass of central Europe. Would silicon from the South Pacific islands or from the plateau basalts, such as those of the Columbia River or of India, agree in atomic weight with these other specimens?

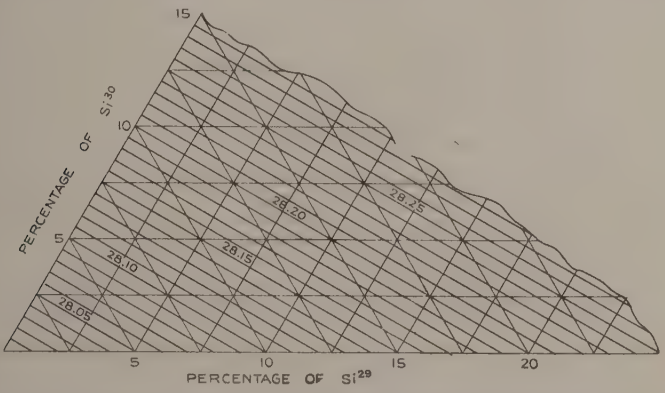


FIG. II.1.—Diagram to illustrate the relation between the atomic weight of a given kind of silicon and the proportions of isotopes Si^{29} and Si^{30} contained in it.

The agreement between terrestrial and meteoritic silicon is so striking that the chances seem rather against our finding any differences, but they are by no means so improbable as to discourage a further search.

POSSIBLE VARIATIONS IN THE COMPOSITION OF SILICA

The possible range of percentage compositions for silica, assuming that it contained only one kind of silicon of exact atomic mass 28, 29, or 30, respectively, in terms of oxygen as 16, are shown in the following table:

Formula	$Si^{28}O_2$	$Si^{29}O_2$	$Si^{30}O_2$
Per cent silicon.....	46.667	47.541	48.387
Per cent oxygen.....	53.333	52.459	51.613

The effect which different proportions of the higher isotopes would have upon the measured atomic weight of silicon, assuming that the atomic masses of the isotopes are exactly 28, 29, and 30, in terms of oxygen as 16, is very simply calculated and is illustrated in Figure II.1, which represents one corner of the triangular composition diagram of the three isotopes.

CHAPTER III. THE ATOMIC CONSTITUTION OF SILICA

The place of silicon and oxygen among the chemical elements

It is no longer open to serious question that matter consists of invisible but real atoms. Our evidence for the existence of atoms—and of electrons—is now quite varied and convincing (see I).[1]

Before discussing the properties of the atoms which make up a fragment or crystal of silica, it will be well to get some idea of the magnitudes involved. This is attempted in Figure III.1, which will serve also to indicate the sizes and designations of the submultiple units of length used throughout this book.[2] The illustrations in the Figure are selected with special reference to the properties of silica.

The currently accepted theory of atomic structure is that of the "nucleus atom". Briefly stated, without discussion of the arguments in its favor, it is as follows:

(A) Every atom of matter may be considered to consist of 2 parts, the *nucleus* and the *external* or *planetary electrons.*

(B) The nucleus consists of a certain number of positive electrical charges or *protons* and a smaller number of *nuclear electrons.*

(C) Practically all the mass of the atom is in the nucleus. The nucleus is the most permanent part of the atom. The mass of the planetary electrons is almost negligible.

(D) The nucleus has a positive electrical charge equal to the difference between the number of protons and the number of nuclear electrons, namely, $P - E$.

(E) The number of planetary electrons is also equal to $P - E$ (when the atom is electrically neutral). This number is the *atomic number* of the element, which is in most cases the same as its ordinal number in the Periodic System as originally arranged on the basis of atomic weights alone, beginning with hydrogen as 1.

The properties of an element are therefore defined by two variables:[3]

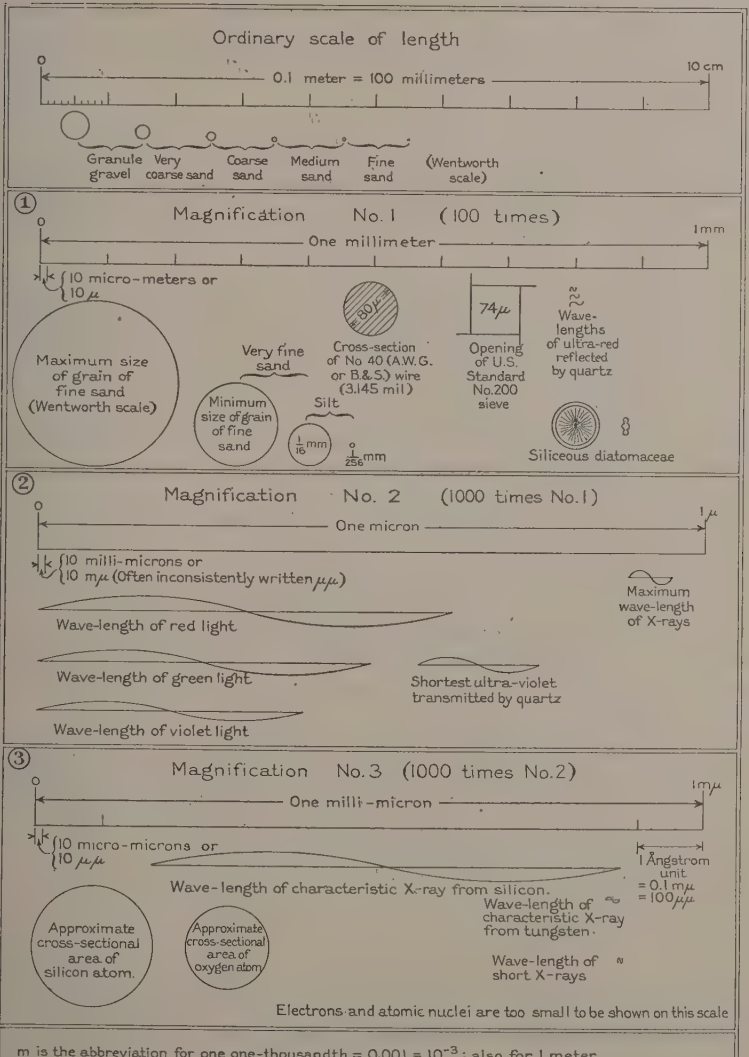
P = the number of protons in the nucleus. This determines the atomic mass, which is the same as the atomic weight when the element is homogeneous and not a mixture of isotopes.

E = the number of *nuclear* electrons. This determines the chemical properties, that is, the position of the element in the Periodic System, since $P - E$ = atomic number.

[1] These text-references are to chapters of this book.

[2] Any terms or abbreviations about the meaning of which there can be any doubt will be found defined in the Index.—The usage of μ and mμ follows the recommendations of the nomenclature committee of the Physical Society of London.

[3] A third variable is also possible, namely, the manner of arrangement of protons and electrons in the nucleus. Radioactive elements which differ only in this respect are known, but there is not yet any evidence of such "nuclear isomerism" among non-radioactive elements.


Ordinary scale of length
0
0.1 meter = 100 millimeters
10 cm
Granule gravel
Very coarse sand
Coarse sand
Medium sand
Fine sand
(Wentworth scale)
1
Magnification No. 1 (100 times)
One millimeter
1 mm
10 micro-meters or 10 μ
Maximum size of grain of fine sand (Wentworth scale)
Very fine sand
Minimum size of grain of fine sand
Silt
1/16 mm
1/256 mm
Cross-section of No 40 (A.W.G. or B.&S.) wire (3.145 mil)
74μ
Opening of U.S. Standard No.200 sieve
Wave-lengths of ultra-red reflected by quartz
Siliceous diatomaceae
2
Magnification No. 2 (1000 times No.1)
One micron
1 μ
10 milli-microns or 10 mμ (Often inconsistently written μμ)
Maximum wave-length of X-rays
Wave-length of red light
Wave-length of green light
Shortest ultra-violet transmitted by quartz
Wave-length of violet light
3
Magnification No. 3 (1000 times No.2)
One milli-micron
1 mμ
10 micro-microns or 10 μμ
1 Ångstrom unit = 0.1 mμ = 100 μμ
Wave-length of characteristic X-ray from silicon.
Wave-length of characteristic X-ray from tungsten.
Wave-length of short X-rays
Approximate cross-sectional area of silicon atom.
Approximate cross-sectional area of oxygen atom
Electrons and atomic nuclei are too small to be shown on this scale

m is the abbreviation for one one-thousandth = 0.001 = 10^{-3}; also for 1 meter.
μ is the symbol for one one-millionth = 0.000,001 = 10^{-6}
mm is therefore 0.001 meter = 1 milli-meter
μm is 0.000,001 meter = 1 micro-meter = 1 micron This is usually shortened to μ.
mμ is 0.001 μ = 1 milli-micron. (The abbreviation μμ, often found, is incorrect.)

FIG. III.1.—Scales of dimensions.

The positions of silicon and oxygen with reference to other chemical elements, as defined by P and E, are illustrated graphically in Figure III.2. (The Figure represents only the lower part of the Periodic System.)

While Figure III.2 shows the relation of oxygen and the silicon isotopes to their neighbors, it does not tell anything of their chemical properties. After all, it is the chemical properties which define an element, and these are determined by the variable $(P - E)$. The striking thing is that the chemical properties do not vary continuously with $(P - E)$, but *periodically*.

The periodicity in which chemical properties recur is not constant, but increases with $(P - E)$. The series begins with a group of 2, followed by two groups of 8, then two groups of 18, then a group of 32 and the beginnings of another group of 32. Now these numbers are proportional to the surface areas of spheres of radius 1, 2, 3, and 4. Hence arises the hypothesis that the external or planetary electrons are grouped into "shells" and that the chemical properties of an element depend almost entirely upon the *outside shell* of planetary electrons. But a subordinate period of 8 is still discernible within the periods of 18 and 32. This leads to the hypothesis that the maximum possible number of electrons in an outer shell of an atom is 8.

The usual way of representing graphically this periodic dependence of chemical properties upon the atomic number $(P - E)$ is to arrange the elements in the order of atomic numbers from left to right, starting a new row at the left at the beginning of each chemical period. In this way we get the Periodic System in its usual form, with vertical columns of elements having similar properties.

A better graphic method, in my opinion, is to measure off atomic number *radially*, and chemical periodicity *angularly*. This gives the plane spiral form of the Periodic System. The jump in the period from 8 to 18, and from 18 to 32, is taken care of by distorting and spreading the spiral at the proper points. This diagram, reproduced in Figure III.3, gives a convenient and instructive grouping of the elements according to their specific properties.

Each numbered point along the spiral represents, of course, only one value of $(P - E)$. If it be desired to represent isotopes,—which are kinds of atoms having the same $(P - E)$ but different pairs of values for P and E,—atomic masses may be plotted perpendicularly to the plane of the diagram and the plane spiral be thereby converted into a spiral helix, with strings of isotopes hanging from points on the helix.

Figure III.3 brings out very clearly the relations of silicon to carbon, on the one hand, and to the four related elements of the "18 sphere," titanium, germanium, zirconium, and tin, on the other. The relationship will be referred to again later in this book.

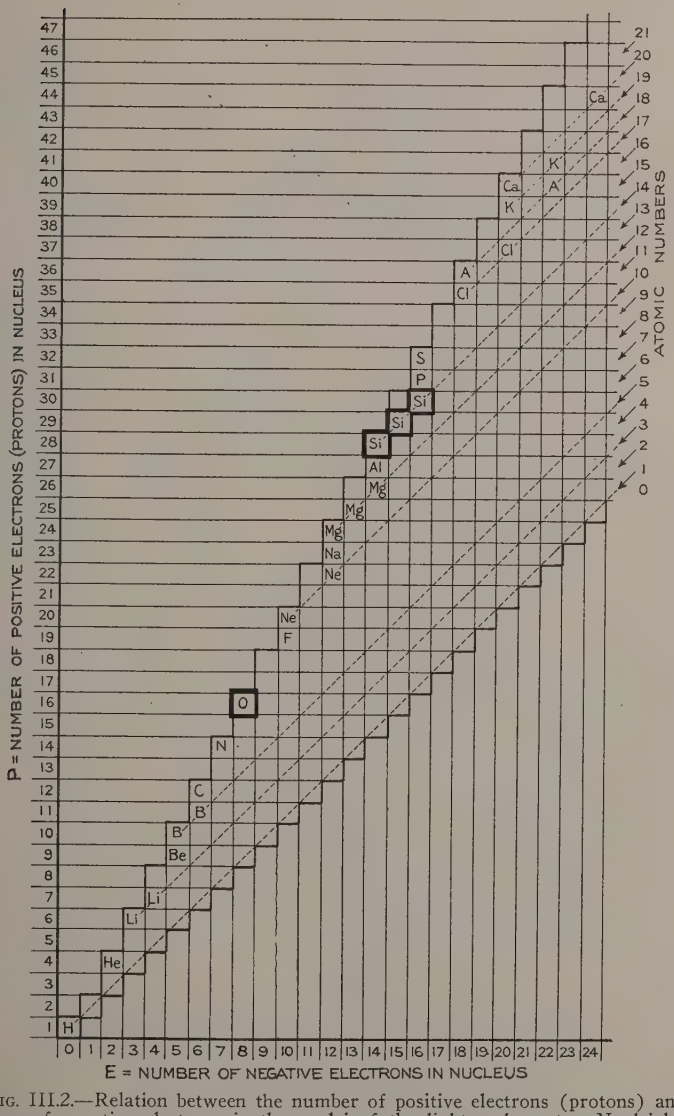


FIG. III.2.—Relation between the number of positive electrons (protons) and the number of negative electrons in the nuclei of the lighter elements. Nuclei having compositions represented by squares below the lower heavy zigzag line can not exist since they could not have a positive charge. Isotopes (atoms having the same value of P-E, and therefore occupying the same place in the Periodic System) must occur along a 45-degree line in this diagram.

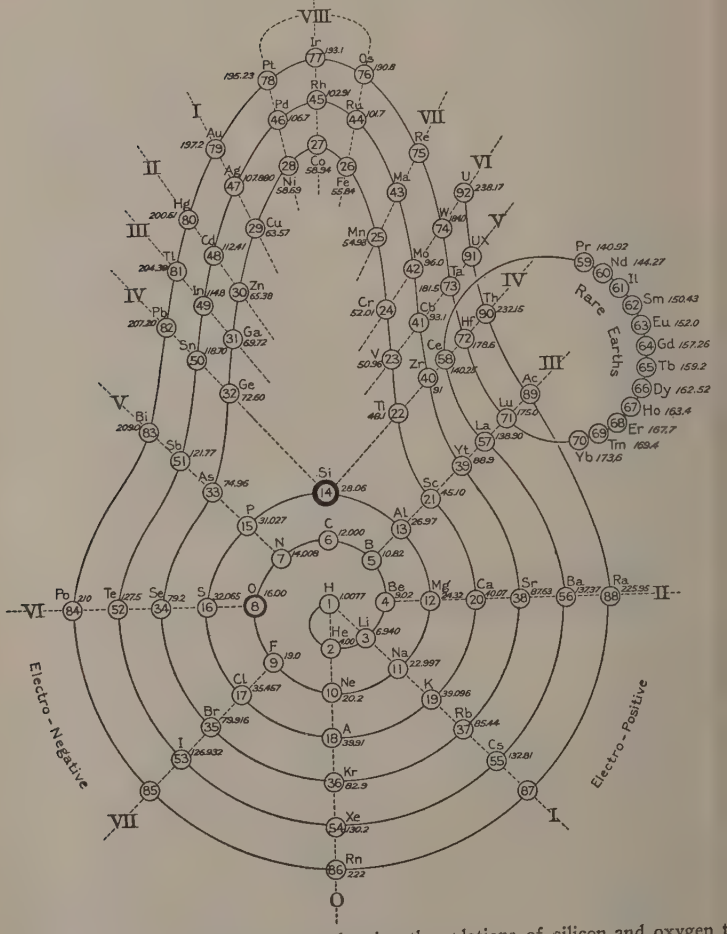


FIG. III.3.—Spiral Periodic System, showing the relations of silicon and oxygen t elements of similar properties.

Theories of the constitution of the free atoms of silicon and oxygen

As already indicated, there is fairly general agreement as to the principle that each atom consists of a dense nucleus and a group of non-nuclear or planetary electrons surrounding it.

As there are three kinds of silicon, an average sample of the element from the Earth's surface will be found to contain three kinds of nuclei. The most abundant kind has a nucleus of mass 28 (relative to oxygen = 16), assumed to contain 28 protons and 14 nuclear electrons, because it has an atomic number $(P - E)$ of 14.

A less abundant kind has a nucleus of mass 29, assumed to contain 29 protons and 15 nuclear electrons because it also has the atomic number 14. A third kind has a nucleus of mass 30, containing 30 protons and 16 nuclear electrons, giving once more the atomic number 14. All three are therefore alike in chemical properties.

There is only one kind of oxygen. Its atomic mass is the standard and is taken as 16; its atomic number is found to be 8. Its nucleus, according to the theory, therefore contains 16 protons and 8 nuclear electrons.

So much for the nuclei. The next question of interest concerns the arrangement of the non-nuclear or planetary electrons, which are equal in number to the atomic number of the element.

At this point recent theories of the atom have diverged radically. The chemist's favorite type of atom, represented usually in terms of the Lewis-Langmuir theory, contains external electrons in relatively fixed positions. They may rotate about their own axes, or oscillate about a mean position, but the facts of chemical valence have inclined the chemist to believe that the electrons cannot be revolving in orbits about the nucleus as the Earth revolves about the Sun. The chemist points out further that such a revolving electron should, according to electromagnetic theory, radiate energy, which it does not do. To explain why the negative electrons do not fall in to the positive nucleus he must, however, postulate some new law of repulsion between electric charges at very small distances.

The physicist, rather than invent a new law of repulsion at small distances, prefers to dispose in some other way of the electromagnetic difficulty of a non-radiating revolving electron and let the revolution of the electron keep it at its proper distance from the nucleus.

The most successful form of revolving-electron theory is that due to Bohr.[4] By applying the quantum theory of emission of energy to systems

[4] Bohr, N., *Der Bau der Atome,* etc., Zeitschr. Physik (1922) **9**: 1-67. For an elementary presentation in English see Kramers, H. A., & Holst, H., *The atom and the Bohr theory of its structure,* (1923, New York). The original theory has now been considerably modified; for a summary with references see Foote, P. D., Amer. Inst. Min. Met. Eng. (1926) paper 1547-D; or Sommerfeld, A., Nature (1926) **117**: 793-795.

of electron orbits, he has succeeded in binding into a uniform whole a considerable variety of facts, and in doing it with such remarkable quantitative accuracy and success that there seems little likelihood that the theory can be displaced by any set of hypotheses based upon "fixed" electrons, although the chemist might do well to hold to his fixed electrons until he sees what will come out of the new quantum mechanics of Born and Heisenberg.

The Bohr atom

The fundamental postulates of the Bohr theory are these:

(1) For each atom or atomic system there exist a number of definite *stationary states* of motion, in which the atom can exist without radiating energy. A finite change in the energy content of the atom can take place only in a process in which the atom passes completely from one stationary state to another.

(2) If such a transition takes place with the emission or absorption of radiant energy, this energy must have a definite frequency, determined by the formula: $\nu = G/h$, in which ν is the frequency, G is the change in energy, and h is the "universal constant" of Planck's quantum theory of energy.

The application of these postulates to the Rutherford nuclear atom with the aid of Bohr's *correspondence principle* linking the occurrence of sets of frequencies in the spectrum with the possibility of certain revolution-frequencies in the atom,—even though these frequencies have nothing to do, under the formula given above, with the frequency of the radiation,—indicates that the most stable state of an atom is characterized by a set of circular and elliptical orbits for the non-nuclear electrons which corresponds remarkably with the periodicities in the atomic numbers already commented upon. In the theory as now revised, each orbit is characterized by a principal quantum number which is related to the size of the orbit, and two secondary quantum numbers which determine its shape and its relation to the other orbits, respectively.

To the chemist's objection that the complicated structure of an organic molecule cannot possibly persist if its parts are in continuous motion the physicist may reply by substituting for the chemist's model, made of firmly fastened wires and balls, a complex link-motion such as can be seen in a locomotive or other complicated piece of machinery, which though continuously in motion, acts as an unchangeable unit and repeats its cycles periodically without the least uncertainty.

Formal theory of chemical combination

We used to say that "the chemical affinity between silicon and oxygen causes them to combine." That was good enough so long as we knew nothing about silica except that it contains silicon and oxygen, but it is too anthropomorphic an explanation to mean anything after we have accum

lated some facts about the ultimate structure of silica.[5] We want an explanation which would have enabled us to predict, in advance of the facts, that silicon would combine with oxygen but not with helium.

The most satisfactory explanation of the combination of atoms to form compounds is in terms of the non-nuclear electrons. We have seen how the recurrence of properties in the Periodic System points to a grouping of those electrons in "shells" if we follow fixed-electron theories, or into "rings," "spheres," or "groups of orbits" under revolving-electron theories, and how in Bohr's theory we even have an explanation of why the groups occur. Whatever be the reason for the groupings of 8, 18, and 32, they are chemical facts which we must take account of.

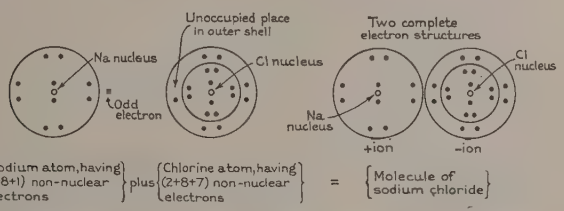


FIG. III.4.—Combination of two atoms by the transfer of one non-nuclear electron.

Each period of the System ends with an inert gaseous element having zero valence, that is, forming no compounds with any other elements. The inert element next after oxygen in the series is neon ($P - E = 10$) supposed to have an inner pair and a complete external octet of planetary electrons. The inert element next after silicon is argon ($P - E = 18$), supposed to have an inner pair and an inner and outer complete octet.

Now imagine two atoms of different atomic number, brought under conditions where they can combine. Suppose one to have an outside group of 8 and one electron to spare, while the other has an outside group of only 7. The electron theory of combination states that the superfluous electron of the first atom is transferred to the second atom, completing its group of 8 or octet, and yielding as a result a positive ion and a negative ion in chemical combination, each part having a complete outside octet. (See Figure III.4.)

Or imagine two atoms each with an outside group of 7. A second formal type of combination consists in these two *sharing* electrons between them, as in Figure III.5. Again the interior portion of each atom is surrounded by a completed octet, and a compound molecule has been formed in the process.

Let us apply this theory of combination to silicon and oxygen, using

[5] Concerning that nearly meaningless phrase, "the force of chemical affinity," see SODDY, *Matter and energy* (1912, New York) p. 107.

first the fixed-electron atom and then the revolving-electron atom. So far as the present discussion is concerned, these are merely two different graphic ways of representing some numerical regularities; we are not really theorizing about the positions or motions of electrons.

Formal theory of the combination of silicon and oxygen

Silicon has 14 planetary electrons. 2 of these form an inner pair, near the nucleus. Outside of this pair is a shell of 8. Outside of this shell is a so-called "incomplete sheath" of 4. Total, 14.

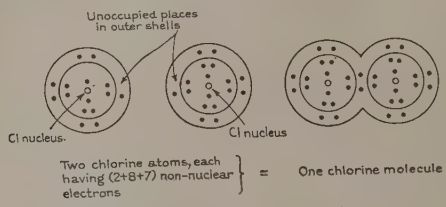


FIG. III.5.—Combination of two atoms by the sharing of a pair of non-nuclear electrons.

Oxygen has 8 non-nuclear electrons. 2 of these form an inner pair. The remainder form an incomplete sheath of 6.

In order to obtain a complete octet or outer shell of 8, the oxygen atom must acquire 2 electrons, while the silicon atom must either acquire 4 or lose 4.

FIG. III.6.—Plane diagram to illustrate the simplest hypothetical form of sharing electrons between silicon and oxygen to form a free molecule of SiO_2.

The simplest way of meeting these requirements is by the sharing of electrons to form a single free molecule of the formula SiO_2, as in Figure III.6. If represented in space, its simplest form would be that shown in Figure III.7.

There is further evidence, found in the regularities of chemical combination, which can be formally expressed in the statement that "electrons tend to group themselves in pairs". In particular, the sharing of electrons between atoms may be assumed to be always in pairs. The octet, instead of being a cube with an electron at each of its 8 corners, might be bet

represented by a tetrahedron with a pair of electrons at each of its 4 corners.

We may strike a compromise between cube and tetrahedron and represent the simplest form of the SiO_2 molecule as in Figure III.8.

Other ways of combining Si and O readily suggest themselves. Thus, the silicon atom might lose all four of its outside electrons, giving up two of them to each of the oxygen atoms. Each atom would thereby acquire

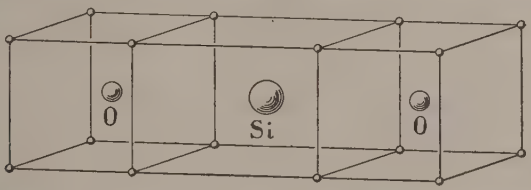


FIG. III.7.—Simplest representation, in space, of the hypothetical manner of sharing electrons between silicon and oxygen shown in Figure III.6.

a complete external octet, and the free molecule would consist of a quadruply charged positive silicon ion and two doubly charged negative oxygen ions.

Various other ways of sharing electrons could be devised if the molecule be supposed to consist of 6, 9, or more atoms instead of only 3. In the absence of information on the true molecular weight of silica in the vapor state it would serve no present purpose to speculate on such forms of combination.

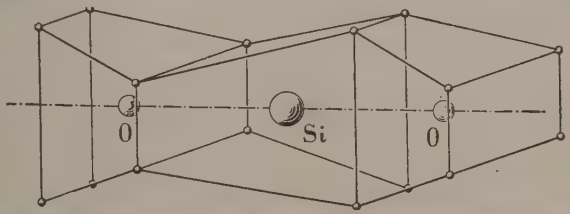


FIG. III.8.—A modification of Figure III.7, taking account of the tendency of electrons to form pairs.

Revolving-electron theory of the combination of silicon and oxygen

We have been talking of the electron structure of a molecule of SiO_2 as if the electrons occupied relatively fixed positions about the nuclei.[6] But, as we have just seen, the evidence strongly favors the view that the electrons revolve about the nuclei in a rather complex set of orbits, some elliptical, some nearly circular.

[6] The expression "fixed electron" is from one point of view a contradiction of terms. We know the electron only through its motions, and to speak of a fixed electron is much like speaking of an inaudible sound or a non-flowing current.

The general principles of the Bohr theory of the atom have already been sketched (p. 34). We may now employ it to describe the manner of combination of silicon and oxygen.

In its most stable state every atom, except that of hydrogen, contains near its nucleus a pair of planetary electrons which revolve in *uniquantous* (German *einquantige*) orbits, designated as orbits of type 1_{11}. The other planetary electrons must have orbits of higher quantum number.

Let us take up first the stable inert atom of the element neon, whose structure tends to be imitated by oxygen when oxygen enters into chemical combination. The stable structure of 10 planetary electrons which characterizes the non-nuclear part of the neutral neon atom consists of the central pair, referred to in the preceding paragraph, together with 8 electrons in *biquantous* orbits. These fall into three groups: two electrons in orbits of type 2_{11}, which are elliptical; two in orbits of type 2_{21}, which are approximately circular; and four in orbits of type 2_{22}, also circular. This set of eight biquantous orbits corresponds numerically to the octet of the chemical theories, but the octet may no longer be considered as a shell of electrons.

The planetary electron structure of oxygen is like that of neon with two of its outer electrons *removed*. It consists, accordingly, of an inner pair of electrons in orbits of type 1_{11}, and two each in types 2_{11}, 2_{21}, and 2_{22}; total, 8.

The silicon structure is like that of neon with four electrons *added*. It consists of the inner pair, moving in uniquantous orbits 1_{11}; eight in the three types of biquantous orbits, as in neon; and four electrons in *triquantous* orbits, of which two are of type 3_{11} and two are of type 3_{21}.

Finally, we may add the argon structure, toward which it is reasonable to suppose the silicon atom tends when it enters into combination. The planetary structure of argon contains the inner pair and the 8 biquantous orbits as in neon, together with 8 triquantous orbits, of which two are of type 3_{11}, two of type 3_{21}, and four of type 3_{22}.

These structures would be difficult to illustrate diagrammatically in a plane figure, for not only do the orbits exist in different planes, but because of precession they are not exactly repeated in space during successive revolutions.

The structures just described are the structures of the atoms in their most stable state. Each atom returns toward this state when its electron orbits are disturbed in an arc, spark, or flame, and it emits its characteristic spectra while so returning.

What changes occur in the orbits when these two atoms, silicon and oxygen, react together we cannot yet surmise, but it is fairly clear that the tendency is for each atom to complete about its nucleus a stable structure of electron orbits. The oxygen atom tends to build up the neon structure, perhaps by taking two electrons from other atoms into orbits of the type 2_{22}. In the same way we may suppose the silicon atom tends toward

the argon structure, by taking on four foreign electrons in orbits of type 3_{22}.

The arithmetical basis of the combination being the same, the formal representation of the bonding of the atoms as used in Figures III.4 to III.7 can be also used, at least as a first approximation, with the Bohr theory.

We have thus a very dependable theory of the constitution of the atoms of silicon and oxygen, together with a reasonable though somewhat indefinite hypothesis as to the manner of combination of silicon and oxygen atoms to form silica. But this has not yet brought us very near the properties of silica in the forms in which we ordinarily see it. The structures just described may do very well for a single molecule of silica floating in space or suspended in a neutral liquid such as liquid helium. They may even approximate the structure in dilute gaseous silica at a temperature not so high as to cause dissociation. But in any real humanly visible form of silica the environment of the molecule may be as important as the interconnection of the three atoms themselves.

The liquid state

We have definite evidence that in the liquid state of silica the unit of structure is larger than the simple atom-triplet SiO_2, but our knowledge of the liquid state of matter in general is too scanty to permit any fundamental statements to be made at this point regarding the structure of liquid silica. Discussion of the manner of linkage of the atoms in the liquid will therefore be postponed until theories of the liquid, glassy, and crystalline states of silica can be discussed.

The crystalline state

There is not yet any general agreement as to the cause of the formation of crystalline solids.

The older theories assumed that the atoms were combined to form molecules in the solid state as well as in the gaseous and liquid states. These molecules were conceived as units, either spherical or of some characteristic constant shape. Some force of attraction between molecules as units then caused them to adhere together in fixed positions, from which they could be released only as a result of the increased thermal agitation due to rise of temperature to the melting-point.

Theories of the geometry of crystals further led to the assumption that a number of molecules could combine to form a so-called "crystal molecule," and that the crystal itself was built up of such crystal molecules as units.

The early X-ray studies on the constitution of binary compounds gave a very different view of the crystalline state. A crystal of sodium chloride was found to consist of row upon row of sodium and chlorine *atoms*.

Every sodium atom is surrounded by 6 equidistant chlorine atoms, a
every chlorine by 6 equidistant sodiums. No definite groupings of at
are discernible. The familiar "NaCl molecule" therefore became a for
abstraction without any concrete experimental meaning in the crystal
state, unless we wish to call the whole crystal one continuous molec

The complexities of organic chemistry make it certain, neverthel
that some kinds of molecules persist in the crystalline state, and can
fused, dissolved, and recrystallized without loss of their identity
molecules.

The present tendency of experimental evidence is toward the view t
the forces which hold the parts together in a crystal, whether those pa
be atoms, atom-groups, or complete molecules, are identifiable with
forces which hold the atoms together in chemical compounds. Wh
permanent molecules are involved, as in the organic compounds, th
molecules are held together in the crystal because of residual electric
magnetic fields coming from the atoms themselves. Where the molec
has disappeared, as in sodium chloride, the process of forming the cry
out of the elements is one and the same with the process of forming
compound.

With which type is silica to be classed? Or has it a character int
mediate between the two? The consideration of this question must
postponed to a later chapter, for the evidence is incomplete and the co
plexities of the polymorphism of silica must first be considered.

Part 2. Phases and their Transformations

Chapter IV. THE PRINCIPAL FORMS

One of the most striking facts about silica is the variety of aspects under which it occurs. For a long time the relations between these forms or modifications were obscure, and it was not until comparatively recent years that we began to get definite information about them. Even now, our knowledge is by no means satisfactorily complete. I find it necessary in this book to refer occasionally to the "better-known" as distinguished from the "less well-known" modifications, a distinction which I hope can be justifiably abandoned in some future edition.

The eight modifications

The eight better-known modifications and their temperature-ranges of stability are as follows:

Low-quartz	Stable at atmospheric temperatures and up to 573° C.
High-quartz	Stable from 573° to 870°; capable of existence above 870° but is then not the stable form.
Low-tridymite	Capable of existence at atmospheric temperatures and up to 117°, but is not the stable form in this range.
Lower high-tridymite....	Capable of existence between 117° and 163°, but is not the stable form in this range.
Upper high-tridymite....	Capable of existence above 163°, and is the stable form from 870 to 1470°; above 1470° is again unstable; melts at 1670°.
Low-cristobalite	Capable of existence at atmospheric temperatures and up to 200°-275°, but is not the stable form in this range.
High-cristobalite	Capable of existence above 200°-275°, and is stable from 1470° to 1710°, its melting point.
Vitreous silica or silica glass	Capable of existence at atmospheric temperatures and up to 1000° or above, where it begins to crystallize with measurable rapidity; but is an unstable, undercooled liquid (a *glass*) at all temperatures below 1710°.

The mutual relations of the eight forms or modifications of silica just mentioned are now fairly well known, and will be considered in the next few chapters.

There remain two other groups of forms of silica which are not yet well defined physically and about which more information is needed. These are:

(1) The cryptocrystalline varieties, the larger part of which are covered by the name *chalcedonic silica;*

(2) The finely divided *amorphous* varieties, such as precipitated sili
These will be described in a later chapter.

The hydrated amorphous forms, such as *opal,* are not included her
they belong with the system $SiO_2:H_2O$, which will not be considered
this volume.

Nomenclature of the modifications

Quartz

The word *quartz* appears to be of provincial German origin, a mine
word coming down from the Middle Ages. It appears in the treatises
Basil Valentine and Agricola after the year 1500. The original form is *Qua*
from which the word has been transliterated into the other languages (quar
kvarts, etc.).

The word has varied much in inclusiveness during its history. Wh
chemical investigation showed the identity of numerous varieties of natu
silica the word "quartz" was extended to cover them all. The discovery
the distinct forms *tridymite* and *cristobalite* detracted but little from its i
clusiveness. The text-books of mineralogy still classify as "varieties of quart
nearly all the natural varieties of silica except the two just mentioned, ev
including some of the partly hydrated varieties.

Modern usage, however, seems to have restricted the meaning to varieti
having certain clearly recognizable crystallographic and optical properti
properties which are generally recognized as distinctive of a crystalline mine
called *quartz.* The varieties which are more difficult to recognize have tend
to revert to their old designations.

The latest phase of the evolution of the term "quartz" is again an exte
sion of meaning, and a wholly unwarranted extension, which will be mention
presently.

Tridymite and cristobalite

The name *tridymite* is the English equivalent of the German *Tridymit.*
is a descriptive name, given by G. vom Rath, who recognized in 1868 t
occurrence of this modification of silica as a natural mineral. He derived t
name from the Greek adjective *tridymos* (τριδυμος), meaning "three-fold
because of the habit of growth of the mineral as "trillings," that is, grou
of three formed by twinning.

The name *cristobalite* is the English equivalent of the German *Cristoba*
The name was given by G. vom Rath, who recognized the mineral in 18
as a new modification of silica. It is a locality name, after the Cerro de S
Cristóbal, from which came the augite-andesite rock specimens in which t
mineral was discovered.

Some of the French mineralogists (Mallard, Lacroix) have spelled t
name *christobalit* and some of the Germans have copied this spelling. The
seems to be no sufficient reason for changing the original form.

The spellings *chrystobalite* and *crystobalite* are purely accidental, but ha
occurred often enough to cause confusion in the chemical and mineralogi
indexes. They are only a natural result of amateur philology and the anarc
caused by phonetic spelling.

High- and low-temperature modifications

When it was discovered that quartz has an inversion point at 573°C at which its symmetry and properties change reversibly, the two modifications were distinguished by means of Greek-letter prefixes, the low-temperature modification being named α-quartz (alpha-quartz) and the high-temperature modification, β-quartz (beta-quartz).

Similar inversions in tridymite and cristobalite were later recognized, and the modifications were designated by prefixes corresponding to those used for quartz, namely, α for the low-temperature modification, and β for the high. When two high-temperature modifications of tridymite were found, the lower was called β_1, and the higher, β_2.

Insisting too much on logic and too little on expediency, some of the German investigators (Boeke, Nacken, Rinne, and others) have within the past few years arbitrarily reversed the previously accepted notation, and now call the high-temperature modification of quartz α, and the low-temperature modification, β. They have likewise reversed the designations of the two forms of cristobalite, and, furthermore, have called α, β_1 and β_2 tridymite respectively γ, β, and α (gamma, beta, and alpha). These changes, if immediately and generally accepted, would bring the nomenclature into accord with the custom which now prevails generally, of naming the modification which is stable at the highest temperature α, the next lower, β, etc. In actual practice the changes have introduced confusion into the current literature on silica—that very worst type of confusion which consists in the interchanging of *A* and *B* or of + and —.

I propose to avoid confusion by calling the modifications "high-quartz" and "low-quartz"; "high-cristobalite" and "low-cristobalite"; "upper high-tridymite," "lower high-tridymite" and "low-tridymite," these terms being abbreviated forms of "high-temperature quartz," etc. Although less compact than the alpha-beta terms, these designations leave no doubt as to what is meant, and, incidentally, relieve the typesetter and proof-reader of some of their worries.

Vitreous silica

Vitreous silica or silica glass has often been called "quartz glass". It is also frequently called "fused silica", "fused quartz", or simply "quartz".

The use of the single word "quartz" to refer to vitreous silica can not be too strongly condemned. It has arisen through carelessness or ignorance and is already causing troublesome confusion.

The word "quartz" is a very old word in our language, and for no one knows how many years *crystallinity* has been its principal connotation. "Rock crystal" has long been one of its synonyms. To have its meaning turned absolutely upside down and inside out, so that it applies to a non-crystalline *glass*, is enough to excite the most hardened philologist or lexicographer.

But this is not the principal objection to the misuse of the word. Chemists and physicists have ignored the protests of philologists and lexicographers before, and have succeeded in placing useful hybrids and monstrosities in the language. But in this case they are working to their own confusion, for crystalline quartz is often used in instruments, especially optical instruments, and so is quartz glass. I feel sure that many, if not most, of the readers of

this book will not be absolutely certain of the complete answer to the following test question: Which of the following-named instruments contain quartz, and which quartz glass; and in what part of the instrument? *Quartz-mercury lamp, quartz spectrograph, quartz fiber, piezo-electric quartz fiber, quartz wedge, bi-quartz wedge.* One of these has been made with both quartz and quartz glass; which one?

German writers have been very careless about this misuse of their corresponding word "Quarz" to mean "Quarzglas," and their usage is partly responsible for the misuse in English. One naturally-to-be-expected result has already followed in Germany; an inexperienced investigator measured the heat capacity of the glass and then compared his results with the published data on crystalline quartz, apparently supposing that he was comparing data on the same substance. The two have, in fact, very different heat-capacity curves.

"Silica glass" or "fused silica" would be the best terms to apply, as all confusion would be avoided. But commercial and industrial custom seems already to have segregated these two terms to mean the opaque, semi-transparent, or silky-surfaced commercial varieties of vitreous silica, and the terms "quartz-glass" and "fused quartz" are now coming to be recognized as referring to the transparent commercial varieties, usually made by the fusion of relatively large fragments of crystal. It is these two terms which have been carelessly abbreviated to "quartz."

I find by correspondence that the manufacturers are quite willing to do their part toward avoiding confusion and ambiguity, and to call the transparent fused product "quartz-glass" or "fused quartz", and that the dealers are willing to follow the lead of the manufacturer. A little cooperation on the part of the user today may avoid a great deal of confusion and misunderstanding in the future, when the progress of invention shall have made quartz and quartz-glass materials of common use.

This matter of nomenclature is by no means to be considered an idle amusement for fastidious and impractical scholars. When the scientist or the engineer calls two different things by the same name, the man in the street assumes that they are in fact the same. We have recently witnessed the widespread disastrous effects of such an assumption concerning wood-alcohol and grain-alcohol.

The commercial distinction just referred to, between "quartz-glass" (the transparent homogeneous product) and "fused silica" (the opaque, translucent, or silky product), is represented in Germany by the two words *Quarzglas* and *Quarzgut,* respectively.

In this book I shall use the term *vitreous silica* for fused or glassy silica in general. Its abbreviated derivative "vitreosil" would have been a useful word to add to the language, had it not been preempted by one of the manufacturers as a trade name. The term "vitreous silica" is not perfect, by any means. For one thing, it is too long; furthermore, petrologists occasionally speak of "vitreous quartz" or "glassy quartz" in describing a rock or rock-section, using these expressions merely to describe the glassy appearance of a fractured surface of crystalline quartz, or to distinguish between a milky or opaque quartz and one that is transparent. Nevertheless, the name "vitreous silica" is not likely to be misunderstood.

Relations between the modifications of silica

An attempt to illustrate graphically the somewhat complicated relations which exist among the eight better-known modifications of silica[1] is shown in Figure IV.1. The solid lines in the figure represent conditions of stability, while the dotted lines represent unstable conditions. The Figure is simply a graphical classification of the eight, so arranged as to show

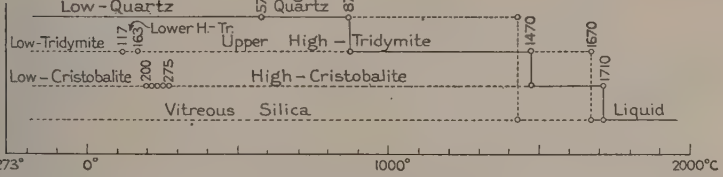


Fig. IV.1.—Graphic representation of the relations between the forms of silica. (Solid lines represent stable states, dotted lines represent unstable states.)

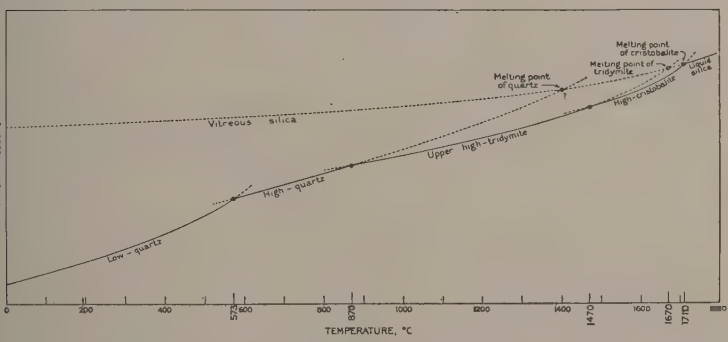


Fig. IV.2.—Imaginary vapor-pressure curves of the more stable modifications of silica. The relative position of the curves indicates the stability of the modifications, though their actual position and shape are unknown.

heir inversion temperatures and their ranges of existence, all at atmospheric pressure.

The method of representation used by Fenner [2] comes a step nearer to a quantitative representation of the relative stability. Fenner's diagram is reproduced in Figure IV.2 with a few minor changes. The Figure shows the relative positions of the curves of vapor pressure against temperature

[1] Sosman, R. B., *The common refractory oxides*, Journ. Ind. Eng. Chem. (1916) 8: 985-990; Trans. Faraday Soc. (1917) **12**: 254-263.

[2] Fenner, C. N., *The stability relations of the silica minerals*, Amer. Journ. Sci. (1913) **36**: 331-384; Zeitschr. anorg. Chem. (1914) **85**: 133-197; preliminary publication in Journ. Wash. Acad. Sci. (1912) **2**: 471-480.

for each of the modifications. The actual vapor pressures are unknown, but we know from thermodynamic principles that the stable modification at a given temperature has the *lowest* vapor pressure. Hence curves can be drawn whose *relative* position expresses the stability, even though

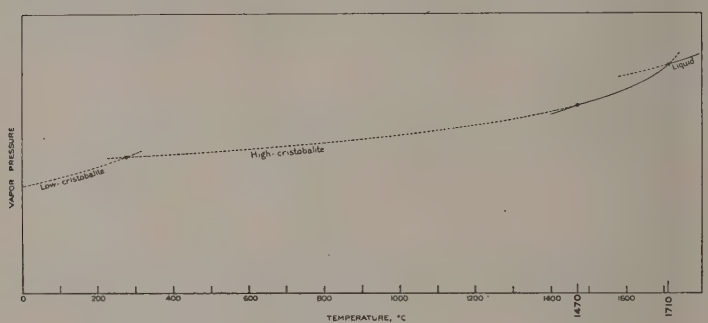


FIG. IV.3.—Imaginary vapor-pressure curves of cristobalite.

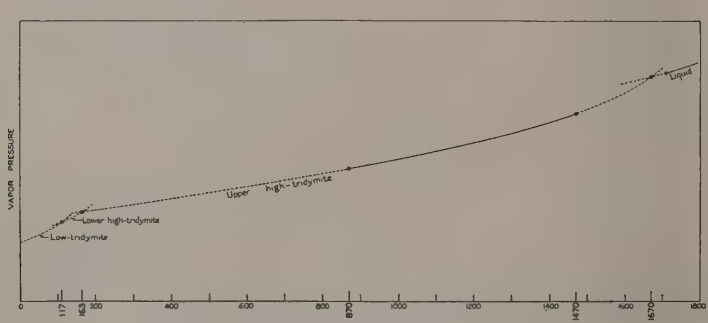


FIG. IV.4.—Imaginary vapor-pressure curves of tridymite.

their actual position and their shape may be unknown. Such are the curves in Figure IV.2.

Figure IV.2 does not show the relative positions of the vapor-pressure curves of low-cristobalite, low-tridymite, and lower-high-tridymite, because the stability of these modifications with reference to one another is not sufficiently known. Individual curves can be drawn for cristobalite only and for tridymite only, and are shown in Figures IV.3 and IV.4, but it is not possible at present to combine these with Figure IV.2.

Quantitative representation of the stability relations

The relative stability of different polymorphous forms varies with the temperature and pressure. If we include with the polymorphous forms the liquid and gaseous states of the substance we shall have all the forms, or *phases,* in which it can exist. At any random temperature and pressure one phase will be found which is more stable than any of the others; and the others, if present, will in time all change into this one, unless the temperature is so low that all change is inhibited.

This stability is determined by the quantity called *zeta,* which is a function of *energy* and *entropy.* Each modification or phase, at the temperature and pressure in question, has a characteristic zeta, and the phase which finally survives is that one whose zeta is the least. (See pp. 348-349.)

A complete statement of the relative stability of the modifications or phases of silica might then be put into graphical form by representing temperature, pressure, and zeta in three dimensions. The zeta of each phase would be represented by a surface. These surfaces would intersect one another, and the intersections would be curves in space, each curve representing the temperatures and pressures at which two phases are in equilibrium. The point at which two such curves intersect would be the single temperature and pressure, the so-called "triple point," at which three phases are in equilibrium.

The intersections of the zeta-surfaces with the plane representing a pressure of 1 atmosphere would be two-dimensional temperature-zeta curves representing relative stability at the constant pressure of 1 atmosphere, the condition in which we are usually most interested. In a general way these curves for silica would look like the curves in Figures IV.2, 3, and 4.

The ideal representation of stability curves just outlined is not yet possible for silica, since the energy and entropy data are not yet sufficiently complete. The data available are more fully considered in Chapter XIX. For the present we can get along with the cruder pictures of Figures IV.2, 3, and 4.

The two types of inversion in silica

In one respect Figure IV.1 gives a truer picture of the relations among the forms than do Figures IV.2 to IV.4, namely, in bringing out the two types of inversion in silica. These may be termed (A) the *sluggish* type and (B) the "prompt-reversible" or *high-low* type.

To the sluggish type belong the inversion of quartz to tridymite at 870°, the inversion of tridymite to cristobalite at 1470°, and the melting of cristobalite at 1710°.

To the high-low type belong the inversions sometimes called the "alpha-beta" inversions: low-quartz to high-quartz at 573°, low-tridymite to

lower high-tridymite at 117°, lower high-tridymite to upper high-tridymite at 163°, and low-cristobalite to high-cristobalite at 200 to 275°.

(A) The sluggish type is characterized by a very slow rate of inversion; it is necessary to hold the substance at a temperature somewhat above (or below) the inversion temperature for a considerable time, sometimes for hours or days, and sometimes to have it immersed in a molten "flux" such as sodium tungstate, in order to have the inversion proceed. It proceeds usually from the free surfaces of fragments. It is possible to heat (or cool) the substance many degrees past the inversion point and to bring it back to the original temperature without causing any change to take place. Finally, the two modifications in question differ considerably in physical properties.

(B) The high-low type is characterized by a very rapid rate of inversion. The change usually occurs promptly as soon as the inversion temperature is reached, and no "flux" is ever necessary. The inversion takes place throughout the whole crystal and does not proceed gradually from the surface inward. The substance can not be heated (or cooled) far past the inversion point without undergoing the change. Finally, the two modifications do not differ greatly in physical properties.

Polymorphism

The marked distinction, just noted, between the two types of inversion raises the question of what we really mean by "polymorphism". Are high-quartz and low-quartz distinct polymorphous forms in the same sense as low-quartz and low-tridymite?

The term "polymorphism" as currently defined and used applies only to the crystalline state of a substance, while the terms "allotropy" and "chemical isomerism" may apply to the liquid and gaseous states as well as the crystalline.

The Century Dictionary (1909 edition, 1914 reprint) defines polymorphism as "The property of crystallizing in two or more fundamental forms". This throws the burden upon the word "fundamental," but from the example there given (diamond, isometric, *versus* graphite, hexagonal) high-low modifications which differ as little as do the two kinds of quartz would not be included.

The Standard Dictionary (1913 revision, 1920 reprint) defines polymorphism as "The property of having or presenting many forms; especially in crystallography, the ability of certain substances to crystallize with different axial ratios without change of chemical composition".

This evidently will not suffice, because mere change of temperature will change axial ratios. The definition would also exclude an isometric substance which remained isometric through an inversion, for its axial ratio has invariably the value 1. It might also experimentally exclude a non-isometric substance, if one were to be found whose axial ratio did not change measurably through an inversion point. (This was at one time thought to be true of high-quartz and low-quartz.)

I would suggest the following definition to cover all the cases likely to be met with: "Polymorphism: that quality of a crystalline substance, having a definite chemical composition, which permits it to appear in modifications belonging to different classes of symmetry or having different axial ratios; changes which are relatively small and at the same time continuous, due to changes of temperature and pressure, are excluded."

If there is a change in symmetry, it is a clear case of polymorphism. If there is not a change of symmetry, but there is nevertheless a discontinuous change in axial ratio with change in temperature, the substance is to be considered polymorphous; likewise if there is an apparently continuous change which is relatively *large,* as in the inversion of β-iron to α-iron. The high-low inversions in silica are all polymorphous changes.

Stability ranges of the principal crystalline forms of silica

As we have seen (p. 48) the prompt-reversible or high-low inversions of silica occur without fail and seldom cause any uncertainty in interpreting experimental results. Furthermore, the changes in symmetry and in other properties at these inversions are not large compared with the changes at the sluggish inversions. It is the sluggish inversions that have caused the most trouble in interpreting the phenomena of the polymorphism of silica, and they will therefore be considered first, the high-low inversions being left for a later chapter.

To emphasize in our nomenclature the distinction just referred to, the crystalline phases of silica between which the inversions are of the sluggish type will be called the *principal crystalline forms.* The phases between which the inversions are of the high-low type will be referred to as *crystalline modifications*; the word *modifications* will also be used where all the crystalline phases are being referred to indiscriminately.

To avoid any confusion which might result from using Figures IV.2 to 4, in which all the modifications are placed on the same footing, I shall refer in the next few pages to Figure IV.5. In this Figure the subordinate effects corresponding to the high-low inversions are conveniently overlooked by starting the curves at 600°.

Range of stability of quartz

Quartz is the stable form of silica from atmospheric temperatures (and probably from absolute zero) up to 870°C $\pm$ 10° (point *b,* Fig. IV.5). This is the temperature of equilibrium between quartz and tridymite at atmospheric pressures. Below 870°, quartz, if under conditions of constant and uniform temperature and pressure, can not be converted into any other form of silica. Above 870° it can not persist as quartz under any conditions of temperature or environment, if the pressure is low.

The experimental data

The most exact determinations of the equilibrium temperature of quartz and tridymite are those of Fenner[3] in 1912, and the temperature 870°C is based on his experiments. He estimates the uncertainty as ± 10°; that is, the true equilibrium temperature is not below 860° nor above 880°.

The experiments consisted in heating quartz or tridymite at temperatures above and below about 900°, in contact with sodium tungstate, in platinum crucibles. The heating was done in a platinum resistance furnace. By observing which of the two forms tended to dissolve and which tended to crystallize at a given temperature, it was possible to find a temperature at which either

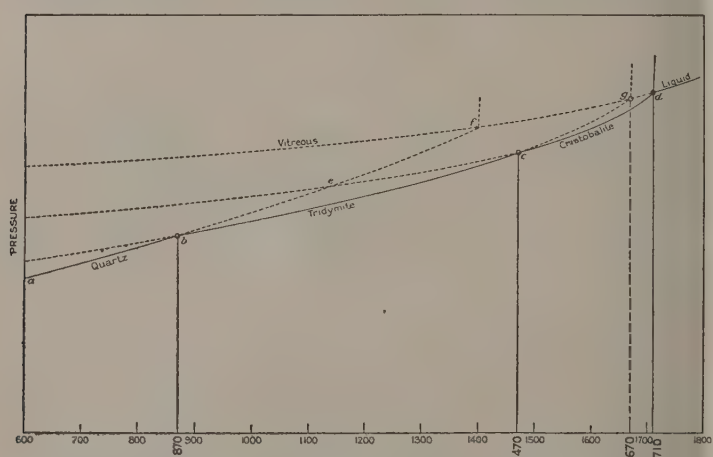


Fig. IV.5.—Imaginary vapor-pressure curves of the principal forms of silica. *ab*, upper part of the stability range of quartz. *bc*, stability range of tridymite. *cd*, stability range of cristobalite. *e*, metastable inversion point of quartz and cristobalite, *temperature unknown*. *f*, melting-point of quartz, *temperature not exactly known*. *g*, metastable melting-point of tridymite.

form seemed about equally likely to appear. This is the temperature of equilibrium between the two.

Day & Shepherd[4] had observed, some years earlier, that vitreous silica changes into quartz in the presence of certain fluxes below 760°, but that tridymite forms from vitreous silica at 800° and higher. They did not observe the fact that this tridymite is not the final stable form at temperatures below 870° but changes further into quartz. They therefore erroneously placed the equilibrium-temperature at about 800°.

[3] Fenner, C. N., articles cited.

[4] Day, A. L., & Shepherd, E. S., *The lime-silica series of minerals*, J. Amer. Chem. Soc. (1906) **28**: 1089-1114.

So far as the records show, Hautefeuille,[5] in 1878, was the first to produce quartz artificially without the aid of water or water solutions. By heating amorphous silica with sodium tungstate for several hundred hours at a temperature not far above the melting-point of the tungstate (700°) he produced doubly-terminated quartz crystals which could be identified by their crystal-forms. When the temperature was raised and lowered over the range 800° to 950°, tridymite was formed above about 850° and quartz below that temperature. Although these temperatures were apparently not measured with exactness, they are entirely in accord with the more accurate measurements of more recent date.

In addition to the experiments just quoted, there are various others in which quartz has been obtained from more or less complex melts, in the absence of water. In all of these the temperatures were known only approximately, so that they do not help much in fixing the equilibrium-temperature of quartz and tridymite, but taking into account the uncertainty of the temperatures, none of the observations is in contradiction to the statement that the stability-range of quartz extends from 870° downward.

The observations include the following:

1899. Morozewicz.[6] Melt having the composition of the rock known as liparite (containing SiO_2, Al_2O_3, MgO, CaO, FeO, K_2O, and Na_2O) with 1 per cent WO_3 added. Quartz obtained after 14 days at about 800-1000° (temperatures not accurately measured).

1899. Bauer.[7] Orthoclase, albite, mica, hornblende, NaCl, K_2WO_4, B_2O_3, and Na_2HPO_4 all melted together. Quartz obtained after 10 hours at varying temperature, maximum 1100°; most of period at 800-900°.

1906. Quensel.[8] Mixture of 74 parts oligoclase and 26 parts silica heated with 1 to 6 per cent WO_3 for 6 to 120 hours at 800-1000°. Temperatures apparently not measured directly, but estimated from melting-points of alloys heated under corresponding conditions. Quartz formed below about 900°, tridymite above about 900°.

Quartz has frequently been crystallized from water "solutions" or obtained from various silicate mixtures in the presence of water.

The earliest experiment of this kind on record was by Schafhäutl,[9] in 1845. To him falls the credit of having been the first to prepare quartz artificially. He obtained it by heating gelatinous silica with water in a "Papin's digester" or autoclave.

During the 80 years that have followed there have been many hydrothermal and aqueo-igneous experiments and silicate syntheses, in which quartz has occasionally appeared as one of the products. The highest temperature at which quartz has been produced in recorded experiments of this kind is about 600°, at which temperature Morey, in the Geophysical Laboratory, has obtained it from water-bearing siliceous melts in steel bombs. The lowest is 90°, the

[5] Hautefeuille, P., *Étude sur la cristallisation de la silice par la voie sèche,* Bull. Soc. Mineral. France (1878) **1**: 1-5; Compt. rend. Acad. Paris (1878) **86**: 1133-1135, 1194-1196.

[6] Morozewicz, J., Tschermak's Min. Petr. Mitt. (1899) **18**: p. 161.

[7] Bauer, K., N. Jahrb. Min. etc. (1899), Beil. Bd. **12**: p. 551.

[8] Quensel, P. D., *Ueber die Bildung von Quarz in Silikatschmelzen,* Centr. Mineral. etc., **1906**: 657-664.

[9] Schafhäutl, Gel. Anzeigen K. Bayer. Akad. (1845) **20**: 557-595.

temperature at which Quensel[10] states that he obtained granules of quartz having a maximum dimension of 5 mm from ordinary glass heated for a week in the presence of Fe_2O_3.

Both of these limits of temperature lie below 870°. Hence the hydrothermal and aqueo-igneous data as a whole are in agreement with the statement that quartz is the stable form of pure silica from 870° down to temperatures approaching atmospheric.

Various observations are on record of quartz which could be seen by the observer to be in course of deposition under known conditions, or which was obviously of such recent or clearly demonstrable origin that the conditions could be inferred with certainty. These observations are all consistent with the foregoing statements as to the stability range. They include such observations as these: quartz[11] depositing from a hot spring at a temperature of 47-51°; and quartz crystals in the midst of cryptocrystalline silica replacing wood whose fiber and structure have been perfectly preserved in the silica.[12]

There are also other data, all equally consistent with an equilibrium-temperature of 870°, on the direct conversion of various forms of silica into quartz. These will be considered in the next chapter.

Range of stability of tridymite

Tridymite is the stable form of silica above 870° ± 10° and below 1470° ± 10°C, at atmospheric pressures (line *bc*, Fig. IV.5). Under conditions of constant and uniform temperature and pressure, tridymite cannot be converted into any other form of silica if the temperature is between 870 and 1470°, and the pressure is low.

1470 ± 10° is the temperature of equilibrium between tridymite and cristobalite.

The experimental data

The only exact determinations of the equilibrium temperature between tridymite and cristobalite are those of Fenner[13] in 1912. He estimates the uncertainty of the point as ± 10°, that is, it is not below 1460° and not above 1480°C. His determinations were made by heating different forms of silica in the presence of fluxes, such as sodium tungstate, at different constant temperatures for various lengths of time, and observing the amount and direction of the change by identifying the products by the aid of their optical properties.

Before the publication of Fenner's experiments in 1912 opinions had differed even as to which of the two modifications, cristobalite and tridymite, is the high-temperature form. Le Chatelier held to the opinion that cristobalite

[10] Quensel, P. D., *Zur Bildung von Quarz und Tridymit in Silikatschmelzen,* Centr. Mineral. etc., **1906**: 728-736.

[11] Beaugey, *Formation du quartz par la source de Mauhourat, à Cauterets,* Compt. rend. Acad. Paris (1890) **110**: 300-302.

[12] Rose, Heinrich, *Ueber die verschiedenen Zustände der Kieselsäure,* Ann. Phys. u. Chem. (Poggendorff), (1859) **108**: 1-40.

[13] Fenner, C. N., articles cited; also *The relations between tridymite and cristobalite,* J. Soc. Glass Technol. (1919) **3**: 116-125.

is metastable at all temperatures, with reference to tridymite, which he considered the only stable phase at temperatures of the order of 1300-1600°. The momentum of his authority, justly based on his eminent work in physics and chemistry and their applications to metallurgy, carried this opinion for some years after Fenner's experiments had shown it to be untenable.

Fenner's original statements as to the relations between the forms are completely in accord with recent experiments by Braesco,[14] a pupil of Le Chatelier, who found that both quartz and cristobalite, when heated with sodium tungstate about 1300-1400° for 4-5 hours, inverted to tridymite which was identified by its dilatation-curve. This same tridymite, on the other hand, when heated at about 1600°, inverted to cristobalite, which was likewise identified by its dilatation-curve.

Furthermore, Endell,[15] in heating specimens of silica brick in the laboratory, has observed the inversion of cristobalite to tridymite at 1450° and the reverse inversion at 1600°.

These facts, with the confirmatory data to be cited below, make it impossible any longer to doubt that cristobalite is the form which is stable at temperatures in the neighborhood of 1500-1600°, while tridymite is the one which is stable above the stability-range of quartz and below the stability-range of cristobalite.

Confirmation of the high-temperature character of tridymite

The fact that tridymite is formed at a higher temperature than quartz and that it can be transformed into quartz was recognized by Hautefeuille[16] in 1878. This relationship has already been discussed (see p. 50).

Additional evidence that tridymite is a high-temperature form was obtained by Le Chatelier,[17] who observed that some silica bricks, made of quartz sand cemented with 2 per cent of lime, after being in use 18 months, were transformed into crystals having a density of 2.26 and a refractive index of 1.48. Mallard[18] confirmed their identification as tridymite by finding characteristic tridymite twins in the same material. Mallard also found that natural tridymite remained unchanged after being heated to a high temperature.

Quensel[19] confirmed the results of Hautefeuille, finding that large 1-cm clusters of tridymite plates were formed at about 950-1000° from amorphous silica heated 4 hours with 5 times its weight of Na_2WO_4. He obtained tridymite again at about 1100° and 1200°.

Schwarz[20] obtained tridymite in the form of well-developed hexagonal plates, in many cases intergrown, by heating water-glass with about three times its weight of sodium phosphate at about 1000° for 6 hours. The soluble salts were then extracted with water, leaving tridymite.

[14] Braesco, P., *Étude des points de transformation par une méthode dilatométrique,* Ann. Physique (1920), **14**: 5-75.

[15] Endell, K., *Ueber Silikaquarzite,* Stahl u. Eisen (1913) **33**: 1770-1775, 1855-1860.

[16] Hautefeuille, P., article cited.

[17] Le Chatelier, H., quoted by Mallard (1890).

[18] Mallard, E., *Sur la tridymite et la christobalite,* Bull. Soc. Franc. Mineral. (1890) **13**: 161-179; Compt. rend. Acad. Paris (1890) **110**: 964-967.

[19] Quensel, P. D., articles cited in notes [8] and [20].

[20] Schwarz, Robert, *Über das chemische Verhalten der verschiedenen Modifikationen der Kieselsäure,* Zeitschr. anorg. Chem. (1912) **76**: 422-424.

The examination of refractories which have been held for long periods at temperatures within the tridymite range also furnishes data confirmatory of the general statements already made. Thus Schulze & Stelzner[21] found that the fireclay muffles or retorts which are used for the reduction of zinc, and which are kept for four to six weeks at temperatures of 1200 to 1300°C, were converted largely into zinc spinel ($ZnO.Al_2O_3$) and tridymite. The tridymite was readily recognizable by its habit of growth in hexagonal plates and in twins and trillings; the crystals varied in size up to 0.3 mm diameter.

Le Chatelier[22] found large plates of tridymite up to 20 mm in diameter in pots of glass of the variety called *quinquet*. The circumstances of the battles in northern France in August, 1914, had caused a batch of this glass, after complete fusion, to be held for 20 days at an intermediate temperature of the order of 800 or 900°. Quinquet is a heavy lead-soda glass with a small percentage of potash, from which pure silica was able to crystallize in stable form under the conditions noted.

Earlier confirmatory observations

Various early observations are on record of the formation of crystalline forms of silica from complex melts at temperatures from red heat to white heat. The temperatures were usually not very exactly known, and the descriptions and data are not always clear, but no significant part of the record is in opposition to the general statements on stability which have been made in the preceding pages.

The first of these was by G. Rose,[23] who in 1869 obtained tridymite plates from melts of adularia ($KAlSi_3O_8$) with sodium ammonium hydrogen phosphate (Phosphorsalz); amorphous silica with the same salt; amorphous silica with wollastonite; and amorphous silica with borax, each heated in a porcelain kiln (perhaps 1450°). A melt of sodium carbonate and silica yielded only spherulites suspended in glass, too fine in grain to be recognized. These were assumed to be tridymite but are just as likely to have been cristobalite.

Marsden[24] has reported the crystallization of silica in the interior of masses of silver, melted in contact with amorphous carbon in Berlin porcelain crucibles and held at a temperature "considerably above the melting point" of the silver for several hours, after which it was cooled slowly. The crystals were of two kinds: (1) hexagonal prisms, mostly colorless and transparent, some of which had the curving forms sometimes met with in quartz; (2) plates or leaves of hexagonal symmetry, colored from light yellow to dark brown. The crystals were insoluble in HCl and in HNO_3, but soluble without effervescence in boiling hydrofluoric acid and in boiling caustic potash solution. They were identified only by this property of solubility, chemical tests having

[21] Schulze, H., & Stelzner, A., *Über die Umwandlung der Destillationsgefässe der Zinköfen in Zinkspinel und Tridymit,* Neues Jahrb. Min. etc., **1881,** I: 120-161, pls. 6-7.

[22] Le Chatelier, H., *Sur la dévitrification du cristal,* Compt. rend. Acad. Paris (1916) **162**: 853-855; Bull. Soc. Franc. Mineral. (1916) **39**: 150-153.

[23] Rose, Gustav, *Über Darstellung krystallisirter Kieselsäure auf trocknem Wege,* Monatsber. K. Pr. Akad. Berlin, **1869**: 449-462.

[24] Marsden, R. S., *On the crystallization of silica from fused metals,* Proc. Roy. Soc. Edinburgh (1880) **11**: 37-40.

already showed that they were not a silicide or other compound of silver. Microscopic sections of the crucibles showed that the original vitreous glaze had been converted into a mass of hexagonal prismatic crystals.

Marsden suggests that the prismatic crystals found in the silver might have been carried in by convection, but that the leaf crystals must have formed out of solution in the metal. The crystals were probably tridymite, but this mode of formation has not been further studied.

Formation of tridymite below 870°

Tridymite has several times been observed as a product of crystallization from water solutions, or from complex melts in the presence of water. All of these were at temperatures below 870°, and thus within the stability-range of quartz. In almost every case, quartz was formed at the same time or by the recrystallization of the tridymite first formed, so that all these occurrences of tridymite can be interpreted as instances of the separation of an unstable phase in accordance with Ostwald's Rule (see p. 61).

Examples of such observations are:

1878. Daubrée.[25] Tridymite deposited in the pores of Roman brick by the waters of the hot springs of Plombières.

1889. Bruhns.[26] Tridymite formed from soda-potash feldspar heated at 300° for 53 hours with HF and water in platinum-lined steel bomb.

Range of stability of cristobalite

Cristobalite is the stable form of silica above 1470° ± 10°, at atmospheric pressures. Its range extends to 1710°, its melting point (line *cd*, Fig. IV.5). Under conditions of constant and uniform temperature and pressure, cristobalite can not be converted into any other form of silica if the temperature is between 1470 and 1710°, and the pressure is low.

The experimental data

The experimental data establishing the true relation of tridymite to cristobalite have already been discussed at pp. 52-54. The upper limit of the range, the melting-point, will be discussed in Chapter VI.

A rather unusual occurrence of cristobalite recently described by Ramdohr[27] appeared to be in conflict with the stability relations discussed in the preceding pages, inasmuch as it was described as a "pseudomorph of cristobalite after tridymite." Now a direct inversion of tridymite to cristobalite, such as would be necessary to produce this pseudomorph, can occur only above 1470°, an utterly improbable temperature under the conditions of occurrence of these specimens; while a replacement of original tridymite by freshly deposited

[25] Daubrée, A., *Études synthetiques de géologie experimentale* (1879, Paris), p. 195.

[26] Bruhns, W., *Beiträge zur Mineralsynthese,* Neues Jahrb. Min. etc., **1889**, II: 62-65.

[27] Ramdohr, P., *Über die Basalte der Blauen Kuppe bei Eschwege und benachbarter Vorkommen und ihren Cristobalit,* Centralbl. Mineral. etc., **1920**: 33-36.

cristobalite also seems rather improbable. A careful reading of the descriptions shows, however, that this is not a case of pseudomorphism in the generally accepted sense, but is merely cristobalite growing in a habit that *imitates* tridymite. This is in entire accord with the known relations and symmetries of the forms. (See, further, p. 205.)

General comments on the experimental work on the sluggish inversions

The sluggishness of the transformations of silica accounts for many otherwise puzzling results of experiment, as well as for numerous misinterpretations of the true relations among the forms.

The views of Le Chatelier on the relative stability of tridymite and cristobalite at high temperatures (see p. 52) proved to be erroneous simply because they were based principally on observations of the behavior of silica in industrial steel and glass furnaces. Now the temperature of such furnaces varies considerably from time to time, and, what is more important, the temperature of a silica brick is usually not uniform over its entire volume. The conclusions drawn from such observations, while valuable, can not compare in reliability with the results of experiments in which the observer has complete control of the time of heating and the constancy and uniformity of the temperature.

The unexpected appearance of unstable phases is also to blame for some misinterpretations and uncertainties regarding silica. No definite and dependable results may be expected unless the temperature is both *constant* and *uniform*. Fenner was able to start with tridymite in a crucible containing sodium tungstate and convert the tridymite into cristobalite within the stability-range of tridymite, simply by having a non-uniform temperature within the crucible. The tridymite dissolved in the hotter part of the crucible and recrystallized in the colder part as the unstable modification, cristobalite.

Historical notes on the classification of the forms

The classification of different "forms" of silica necessarily had to await the recognition of silica as a distinct substance. To the Greeks, rock crystal, amethyst, chalcedony, and opal were different minerals, as different from one another as orthoclase, muscovite, and quartz seem to us.

It was not until the latter half of the eighteenth century that the essential identity in composition of these different minerals began to be recognized. In 1783 Romé de l'Isle stated definitely the opinion that rock crystal, quartz, amethyst, quartzite, agate, etc., are all forms of the same substance, although the composition of that substance, in terms of "Kieselerde," "Thonerde," etc., was still in doubt.

The next step was the proof that these minerals are essentially pure Kieselerde; and this could soon be followed by Berzelius's proof (1824) that Kieselerde itself is a compound consisting of the elements silicon and oxygen

Early classifications

Berzelius distinguished two kinds of silica:

"^{b}Kieselsäure," which is soluble in water and dilute acids;
"^{a}Kieselsäure," which is insoluble in water and dilute acids.

The first of these kinds is transformable into the second. We recognize now that this distinction is not fundamental, but depends on many complex conditions.

H. Rose [28] classified silica into two kinds, fundamentally on the basis of density. "Crystalline silica" has a density of 2.65, while "amorphous silica" has a density of 2.2. The second class could "under certain circumstances" have a density as high as 2.3.

In 1858 Jenzsch [29] thought he had evidence that the so-called "Fettquarz" found in many melaphyre rocks was really a second crystalline form of silica, and he named his supposed new form "Vestan." The distinction was based principally upon cleavage and external form, since the density, hardness, and general chemical behavior were not very different from those of quartz.

A few years later Jenzsch [30] proposed the name "amorphe Kieselerde" for a supposed new amorphous silica of density 2.6, produced in the form of a fine white powder by the weathering of chalcedony and opal. The limits of density actually determined on material from 4 localities were 2.591 to 2.647.

There is no reason to suppose that these products were anything else than very finely divided quartz or chalcedony mixed with a little opal.

In the year 1868, then, silica was generally recognized to exist in the single crystalline form *quartz*, of high density; *chalcedony* being considered to be a variety of quartz. Silica was also recognized to exist in a single amorphous form of low density, 2.2 to 2.3, of which *opal, hyalite, vitreous silica, sublimed silica,* and *silica of organic origin* were considered varieties.

Discovery of tridymite

In this year (1868) vom Rath [31] announced his discovery of a new crystalline form of silica, which he named *tridymite*. It was found in fractures and clefts of a specimen of trachyte, an effusive igneous rock, sent to him from Cerro (Mount) San Cristobal, near Pachuca, about 60 miles northeast of Mexico City. It occurred as colorless crystals 1 mm or less in diameter.

Once identified and described, the new mineral was found in a considerable number of occurrences, chiefly in eruptive rocks, in France and Germany. Furthermore, G. Rose [32] recognized it as the form of silica which he had obtained in 1867 in the shape of minute crystals, by the fusion of feldspar and

[28] Rose, Heinrich, article cited in note [23].
[29] Jenzsch, G., *Die krystallisirte Kieselsäure ist dimorph,* Ann. Phys. u. Chem. (Poggendorff) (1858) **105**: 320-329.
[30] Jenzsch, G., *Ueber amorphe Kieselerde,* same (1865) **126**: 497-506.
[31] vom Rath, G., *Vorläufige Mittheilung über eine neue Krystallform der Kieselsäure,* Ann. Phys. u. Chem. (Poggendorff) (1868) **133**: 507-508. Monatsb. K. Pr. Akad. Wiss. Berlin, **1868**: 201-206.
[32] Rose, Gustav, *Über Darstellung krystallisirter Körper mittelst des Löthrohres,* etc., Monatsb. K. Pr. Akad. Wiss. Berlin, **1867**: 129-147, p. 140.

other silicates in the phosphate bead ($NaNH_4HPO_4$) before the blowpipe, verifying this by preparing it in larger crystals.[33]

Discovery of cristobalite

One of the excursions to which vom Rath had looked forward for years was a visit to the mineral locality at Pachuca, Mexico, whence his original tridymite specimens had been sent to him. This desire was finally gratified on the occasion of his visit to America in 1884. He made a side trip to Pachuca and the Cerro San Cristobal, and while examining the tridymite-bearing rock there he noticed some white crystals having isometric symmetry, which did not correspond in properties to any known mineral.

This discovery was announced at Bonn[34] in 1884, but details of the properties of the new mineral were not published until 1887, when the name *cristobalite* was proposed for it.[35] It consisted of octahedral crystals about 2 mm in diameter, and spinel-type twins up to 4 mm. So small an amount of material was available that only 81 mg could be taken for analysis; this yielded 91.0 per cent SiO_2, 6.2 per cent Fe_2O_3 and Al_2O_3, no CaO. The iron and alumina were evidently admixtures, so the evidence was good that the essential mineral consisted of pure silica.

Vom Rath did not feel justified in excluding entirely the possibility that his proposed new mineral might be only a pseudomorph of silica after some other mineral. But in considering what this original substance might have been, he found that only spinel, faujasite (a zeolite), or tridymite in its mimetic cubic habit, seemed admissible possibilities, and all of these were shown to be improbable as original crystals of a silica pseudomorph. Optical examination of the material by M. Bauer[36] also indicated that it was probably not a pseudomorph. The new mineral therefore appeared to have a good chance for survival.

After cristobalite had been discovered, described, and named by vom Rath, it appeared that it had been observed before on several occasions without being recognized as a new mineral.

Donato Garcia is said by Andres del Rio[37] to have found 3-mm octahedral crystals of silica in the neighborhood of Madrid, about the year 1800. They were classed by Rio as a variety of opal. Wolf[38] in 1868 observed "snow-white octahedra, hard, with glassy luster, infusible, and insoluble in acids" on inclusions in the lava of Ettringen. Lehmann[39] observed these octahedra, and to spinel-like twins, in the same lava, accompanying tridymite. Both authors thought that the crystals might be spinel, but had not enough material for their further study.

[33] Rose, G., article cited in note[23].

[34] vom Rath, G., (Letters from Mexico), Sitzungsb. Niederrhein. Ges. Natur-u. Heilkunde Bonn, **1884**: 100-126, p. 112.

[35] vom Rath, G., *Ueber Cristobalit vom Cerro S. Cristobal bei Pachuca (Mexico)*, Neues Jahrb. Min. etc., **1887**, I: 198-199.

[36] Bauer, M., Neues Jahrb. Min. etc., **1887**, I: 199-200.

[37] Rio, Andres del, *Elementos de orictognosia, Parte practica,* (1832, Filadelfia), p. 270.

[38] Wolf, Th., Zeitschr. Deut. Geol. Ges. (1868) **20**: p. 16.

[39] Lehmann, J., Verh. Naturhist. Ver. Preuss. Rheinl. u. Westfalens (1874), **31**: p. 35.

The announcement of two new crystalline forms of silica, both relatively rare so far as petrographic knowledge then went, seems to have left chemists and mineralogists a bit skeptical. The two forms had nearly the same density and were crystallographically allied. Tridymite was generally admitted to be an independent form but the opinion was natural and was several times expressed that cristobalite was only tridymite under an obscure habit. The common grouping of tridymite with exterior faces making almost exactly the angle of a regular octahedron emphasized this view. (See also pp. 56 and 199.)

It was Mallard,[40] in 1890, who really put cristobalite on its feet and gave it a standing among the well-recognized minerals. His measurements of optical properties, and especially his discovery of a high-low inversion, proved that it was a form distinct from tridymite. Later investigations have supported Mallard and vindicated the original judgment of vom Rath.

Mallard thus revived and strengthened the old classification of silica into two families (see p. 57), but restricted it to the crystalline forms. *Silica of high density* would include quartz and chalcedony as before, while *silica of low density* would include tridymite and cristobalite. A parallel distinction, according to Mallard, is that the first group of forms is produced at relatively low temperatures, the second at relatively high temperatures.

Almost coincident with these researches by Mallard came Le Chatelier's discovery in 1889 of the high-low inversion of quartz (see p. 124), so that by 1890 the materials were all prepared for the outline of the principal modifications of silica as now understood, and as presented at the beginning of this chapter. The most important advance of recent years is marked by the publication in 1913 of the researches of Fenner, which cleared up the disputed questions concerning the stability relations of the principal forms and uncovered some new facts about the high-low inversions, which will be considered in Chapter VII.

[40] MALLARD, E., article cited in note[18].

Chapter V. THE SLUGGISH INVERSIONS

Having outlined the conditions of stability of the principal forms, we may consider the phenomena of the sluggish inversions in greater detail, and especially the rates of change as influenced by temperature and other variables.

Number of permutations

Between the 3 principal forms: quartz, tridymite, and cristobalite, taken two at a time, there are possible 6 permutations, as follows:

(1) Quartz to tridymite
(2) Quartz to cristobalite
(3) Cristobalite to tridymite
(4) Tridymite to cristobalite
(5) Tridymite to quartz
(6) Cristobalite to quartz

If we take no account of chemical facts, all of these 6 permutations are logically possible within each of the 3 temperature-ranges of stability of silica, making 18 possibilities to consider. Experimental fact cuts this number down to the 9 shown in the tabulation below:

	Quartz	Tridymite	Cristobalite
Below 870°	No change	To cristobalite To quartz	To tridymite To quartz
870 to 1470°.....	To cristobalite To tridymite	No change	To tridymite
1470° to melting point	To cristobalite	To cristobalite	No change

General principles

Three principles need to be kept in mind in studying the transformations of silica:

(1) Under conditions of constant and uniform temperature and pressure, a stable form will show no tendency to change into an unstable form.

(2) Under conditions of constant and uniform temperature and pressure, an unstable form may change either to the form stable at that temperature, or into some other *unstable* form.

(3) Under conditions where the temperature is not constant, or is not uniform over all parts of the material under observation, almost any form or combination of forms, stable or unstable, may be found.

There is nothing mysterious about these principles. Number (1) is simply a definition of stability. Numbers (2) and (3) are a restatement

of the fact that the inversions in question are very sluggish, coupled with another fact, often noted in connection with polymorphous inversions of all kinds, that when a transformation is in progress the less stable modification is more likely than the more stable to appear first. This latter fact was put into a more quantitative form by W. Ostwald,[1] and is often called "Ostwald's Rule": "In all reactions the most stable state is not straightway reached, but the next less stable, or that state which is the least stable of the possible states." The rule does not always hold, however, as will be seen from the data on the transformations of silica.

Permutation (1): Quartz to tridymite

Temperature ranges

Below 870°, as we have already seen, principle number (1) applies; that is, under conditions of constant and uniform temperature and pressure, quartz, whether dry or in contact with any kind of a melt or solution, can not be converted into any other crystalline form of silica.

Above 1470°, in the range where cristobalite is stable, the formation of tridymite as an intermediate unstable phase, though logically possible, and even to be expected under "Ostwald's Rule," has never been observed with certainty. It is true that tridymite has been found in siliceous mixtures which had been heated to temperatures above 1470°, but every such instance can be explained as due to transformations occurring while the material was passing through the range of temperature *below* 1470°.

We have left to consider, then, only the *range 870 to 1470°*.

Two cases need to be separately considered: (A) the transformation of quartz in the pure dry state; (B) the transformation of quartz in the presence of a melt ("flux") or solution.

Transformation in the pure state

The direct conversion of quartz into tridymite by heat alone has not been definitely proved. It may sometimes occur, but it is certainly not the change which is usually observed. When heated to temperatures between 870 and 1470° without a flux, quartz is nearly always found to invert not to tridymite, but to cristobalite, an example of principle (2), page 60. This cristobalite can then be caused to invert further into tridymite, the stable modification in this range, as described in a later section (see p. 73).

Ferguson & Merwin[2] heated clear quartz crystals for 144 hours at temperatures ranging from 1300° to 1400°C, and obtained, from some of the

[1] Ostwald, Wilhelm, *Studien über die Bildung und Umwandlung fester Körper*, Zeitschr. physik. Chem. (1897) **22**: 289-330, p. 306.

[2] Ferguson, J. B., & Merwin, H. E., *The melting points of cristobalite and tridymite*, Amer. J. Sci. (1918) **46**: 417-426.

larger grains, lumps of cristobalite having hard clear nuclei of *tridymite*. Now quartz, in inverting to cristobalite, usually transforms completely into a fine-grained aggregate. It seems unlikely, therefore, that these clear tridymite grains could have been formed secondarily through the recementing of the fine-grained cristobalite. The evidence thus points to the direct conversion of these cores from quartz into tridymite.

On the other hand, there remains the possibility that all of the quartz first effloresced to cristobalite, and that the cristobalite then vaporized little by little, moving but a short distance and then recondensing as tridymite, in this manner building up the solid nuclei.

Day, Shepherd & Wright,[3] in 1906, reported the formation of "tridymite" direct from quartz at temperatures of 1100 to 1600°. As the material was very fine-grained they depended entirely upon its optical properties for identification. Through the unfortunate publication of an erroneous or misprinted value for the birefringence of cristobalite by Mallard in 1890, the possibility that the quartz-inversion product might be cristobalite was at first overlooked. Lacroix called attention to the error in Mallard's data and a re-examination of the supposed tridymite by Wright showed it to be cristobalite.

G. Rose[4] in 1869 reported the conversion of quartz, in the form both of euhedral crystals and of massive quartz in granite, into "tridymite." The existence of cristobalite was unknown at that time, and no optical data are given which would show that the product was anything else than cristobalite.

Transformation of quartz into tridymite in the presence of other substances

For the ready and sure conversion of quartz into tridymite the presence of some other substance or substances is necessary. The effect of the added substances seems to be principally the forming of a liquid melt or "flux," whose presence greatly accelerates any changes and may lead directly to the formation of the stable phase.

Phenomena of the inversion

The transformation of quartz into tridymite in the presence of a flux in the range 870° to 1470° may occur in either of two ways. The atoms or atom-groups may simply rearrange themselves into the tridymite structure; or they may pass into solution in the molten flux and then crystallize out again at another place as crystals of tridymite.

The second of these ways is the one which has been most often observed, especially in impure materials such as silica brick. Tridymite crystals are seen in course of formation in the midst of small portions of the fluxing liquid, while at other points quartz crystals are in course of dissolution.

[3] Day, A. L., Shepherd, E. S., & Wright, F. E., *The lime-silica series of minerals*, Amer. J. Sci. (1906) **22**: 265-302.

[4] Article cited in IV, note [23].

The process of inversion of quartz to tridymite in the presence of a liquid is not, however, always a process of solution and recrystallization. Individual particles of quartz seem to be converted directly into tridymite without moving from their positions. The role of the liquid in this process is not clear. (See further details below.)

Fenner [5] observed that when quartz inverts to tridymite in the presence of sodium tungstate, many of the quartz grains retain their individuality but are gradually replaced by an aggregate of tridymite crystals of random orientation. When the replacement is incomplete, irregular nuclei of quartz remain, surrounded by tridymite which occupies the space formerly filled with quartz.

Chrustschoff [6] followed the stages of the transformation of the quartz in quartzitic granites, gneisses, and schists, when immersed in about an equal weight of molten basalt or melaphyre. His temperatures were not measured. He observed the finely and irregularly fragmented glass-saturated quartz particles dividing into straight-sided, often hexagonal, polygons, which were nearly isotropic except for isolated strongly birefringent residues of quartz. The fine cracks then disappeared; the polygons and cloudy quartz areas were replaced by clear, rounded, overlapping fish-scales of tridymite. The glass which formerly occupied the fine cracks was now inclosed as lines or clumps of glass particles within the finished tridymite.

Clews & Thompson,[7] heating powdered quartz in molten sodium chloride at 1000°, observed the growth of tridymite in the form of rods, wedges, and thin hexagonal plates with well-defined boundaries. They are of the opinion that the conversion in this case is through actual solution of the quartz in the sodium chloride, and redeposition as tridymite, because when only a relatively small quantity of salt is used the conversion is much retarded. 24 hours' heating, for example, with only a little salt, lowers the density to 2.451, and 45 hours' heating to 2.418, representing only about two-thirds conversion, while with an excess of salt such that it forms a liquid surface above the quartz in the crucible the inversion is complete within 51 hours.

Parravano & Rosselli del Turco [8] found only a few minute crystals of tridymite in a natural quartzite mixed with 1.5 per cent CaO according to the usual process of manufacture of silica brick, and fired for 12 days, rising to a maximum temperature of 1430°C. Addition of another 1.5 per cent CaO had no appreciable effect on the transformation.

They observed that the few minute grains of tridymite which formed in the quartzite mixed with 1.5 per cent CaO were clustered about grains of iron oxide which had originated from the oxidation of fragments of iron derived from the pulverizing mill.

A similar mixture to which Fe_2O_3 was added differed from other mixtures

[5] Articles cited in IV, note [2].

[6] Chrustschoff, K. v., *Ueber gelungene Versuche zur Darstellung des Quarzes auf nassem und des Tridymits auf trockenem Wege,* Neues Jahrb. Min. etc., 1887, 2: 205-208.

[7] Clews, F. H., & Thompson, H. V., *The interaction of sodium chloride and silica,* J. Chem. Soc. London (1922) 121: 1442-1448.

[8] Parravano, N., & Rosselli del Turco, C., *L'influenza di alcuni fondenti sulle trasformazioni del quarzo,* Gazz. chim. ital. (1923) 53: 249-257. Atti R. Acc. Lincei, Rend. (1923) 32, I: 9-14.

containing P_2O_5, WO_3, or extra CaO, in that the masses of cristobalite, which filled the spaces between unaltered quartzite, contained fine crystals of tridymite in much greater number than did the other mixtures. These crystals formed a fine network in the mixture containing 1.5 per cent Fe_2O_3.

It appears possible, then, that Fe_2O_3 has some specific action in promoting the crystallization of tridymite, not possessed by certain other oxides.

Holmquist [9] has observed the transformation in silica brick. He finds tridymite growing only in the small "rivulets" of liquid (glassy) silicates formed by the fusing together of the various impurities, or in the masses of cristobalite which have formed directly from the quartz, and which were thought at first by several investigators to be fused or vitreous silica.

It is probable that these cases observed by Parravano and by Holmquist, as well as other similar occurrences of tridymite, are cases of indirect conversion of quartz into tridymite, the first product having been either cristobalite or a liquid silicate.

Speed of the inversion

The speed of the direct inversion of quartz into tridymite, in presence of sodium tungstate as a flux, is very slow near the inversion point, but increases as the temperature rises higher above 870°. At 875° only a small proportion of the quartz is converted after 24 hours. At 1000° the conversion is complete within 118 hours, and at 1300°, within 3 hours.[10] With sodium chloride as a flux the conversion at 1000° is complete [11] within 51 hours.[12] The rate of inversion seems not to be influenced by fine grinding of the quartz.[10]

Clews & Thompson [12] studied the transformation at 1000° ± 20°, using pure sodium chloride as a flux. The speed of conversion of powdered quartz at this temperature is indicated by the following results:

Period of heating	Density
0	2.634 (at 9.2°)
25¼ hr.	2.317 (at 15.5°)
51¼ hr.	2.285 (at 14.1°)
79½ hr.	2.284 (at 15.5°)

Permutation (2): Quartz to cristobalite

Temperature ranges

Below 870° quartz is the stable modification of silica. No amount of heating, whether dry or in the presence of a melt or solution, can make any change in it if the temperature be uniform and constant so that tem-

[9] Holmquist, P. J., *Über die Bildung von Tridymit und Cristobalit in Quarz-Ziegeln*, Geol. Fören. Förh. (1911) **33**: 245-260, pls. 2-4.
[10] Fenner, C. N., articles cited in IV, note [2] (1913).
[11] Correspondence with Messrs. Clews & Thompson.
[12] Clews & Thompson, article just cited.

porary solution and redeposition are prevented. *Above 1470°*, on the other hand, cristobalite is the stable modification, and the transformation of quartz into cristobalite is the direct and stable inversion.

But if the temperature be lowered this transformation does not cease sharply at 1470°. If no flux is present, it continues in the *range 870° to 1470°*, as already mentioned, even though tridymite is then the stable modification. This is an example of principle (2) (see p. 60), a case of the intermediate formation of an unstable phase.

Quartz, when heated alone, may thus be expected to change into cristobalite at any temperature above about 1000°, though the change is a permanent one only above 1470°.

The metastable inversion temperature

From the curves of Figures IV.2 and IV.5 it will be evident that there is no stable equilibrium and therefore no true inversion temperature between quartz and cristobalite at atmospheric pressure. A metastable equilibrium is, however, possible, and hence a metastable inversion temperature at which quartz and cristobalite would be in equilibrium and would have the same vapor pressure, provided tridymite did not appear. This is the point *e* in Figure IV.5.

This metastable inversion temperature must lie below 1250°, since quartz changes to cristobalite at an appreciable rate at that temperature, but there is no evidence by which it may be located with exactness. If a flux is used, to accelerate the transformation of the quartz, tridymite is obtained and not cristobalite, hence the flux is of no assistance in finding the temperature of the metastable inversion-point.

Wietzel[13] has constructed an *"A-U* diagram" (curves of the change of total energy against the change of maximal work or Helmholtz free energy, with temperature) for the reaction quartz ⇄ cristobalite. This construction gives to the maximal work the value zero at about 1400°C. This temperature should therefore be the metastable inversion temperature of quartz to cristobalite. The estimate is subject to a large uncertainty, however, as will be discussed more fully in Chapter XIX; it is evidently too high, since quartz is known to change into cristobalite at as low a temperature as 1250°. The most that I should venture to say on the basis of the thermodynamic data alone is that cristobalite is certainly more stable than quartz above 1500°C, and that, if the formation of tridymite were prevented, quartz would probably be in equilibrium with cristobalite at a temperature somewhere below 1400°C. These facts we already knew, so that the thermodynamic calculation has not helped much. But when more exact thermal data shall have become available, it is likely that the thermodynamic calculation will give the metastable inversion temperature more accurately than it can ever be determined by direct experiment.

[13] Wietzel, R., *Die Stabilitätsverhältnisse der Glas- und Kristallphase des Siliciumdioxydes,* Zeitschr. anorg. allg. Chem. (1921) **116**: 71-95.

Phenomena of the inversion

There is evidence that quartz, in changing to cristobalite, does not always go directly into the cristobalite form, but first passes through a stage of fusion.

It is possible that the transformation always follows this course. On the other hand it is likewise possible that external or internal conditions may be varied so as to cause the transformation to occur by either route: sometimes by way of this preliminary fusion, sometimes by direct rearrangement of atoms or atom-groups. The evidence is not yet sufficient, and is further confused by the fact that very fine-grained cristobalite is sometimes indistinguishable, under the microscope, from vitreous silica. This question of the fusion of quartz will be considered more fully in Chapter VI.

Whether the change occurs by way of preliminary fusion or by direct rearrangement of atoms, it remains true that the change as ordinarily observed on the larger grains and crystals begins at exposed surfaces and grows inward. There is never any starting of cristobalite nuclei in the interior of a continuous homogeneous fragment of quartz.

The heating of a homogeneous quartz crystal to a temperature above its true upper limit of stability, that is, to above 870°, seems to have no effect on its properties if it is cooled again before any inversion to cristobalite or tridymite has started. I have heated a crystal about 5 cm long, immersed in molten tin, to 1300°, and have brought it back to atmospheric temperature again with perhaps 10 or 15 cracks, 5 to 10 mm apart, the crystal remaining otherwise unchanged. Rieke & Endell [14] observed that several heatings in a porcelain kiln (1450°) left a quartz crystal from St. Gotthard unchanged in appearance except for a few cracks. Rose [15] found that the density of a quartz crystal did not change by as much as 0.1 per cent after heating in a porcelain kiln.

Holmquist [16] stated definitely in 1911 that fusion of the quartz precedes its conversion into cristobalite and tridymite in silica bricks. It turned out later, however, that what he supposed to be vitreous silica was in reality cristobalite. Glass was also present, to be sure, but it was formed by the combination of silica with lime or other impurities and by the fusion of the resulting mixture of compounds, out of which tridymite subsequently crystallized.

Speed of the inversion of quartz to cristobalite

The rate of transformation of quartz into cristobalite is strongly influenced by two factors: (1) the state of subdivision of the quartz, and (2) the temperature.

[14] Rieke, R., & Endell, K., *Die Volumänderung einiger keramischer Rohmaterialien beim Brennen. II. Kieselsäure,* Silikat-Zeitschr. (1913) 1: 48-52, 67-72, 85-89.
[15] Rose, H., article cited in IV, note [13] (1859).
[16] Article cited in note [9].

The state of subdivision and the degree of twinning of quartz have a very large effect upon its rate of transformation to cristobalite. A large homogeneous untwinned crystal transforms extremely slowly. Without change of temperature the same crystal may be made to change much more rapidly by reducing it to a fine powder. Finely twinned vein quartz, even though in large fragments, transforms more rapidly than a finely powdered untwinned crystal, while powdering this twinned quartz produces an increase of rate even above that characteristic of the large twinned fragments. These relations will be more fully discussed in the chapter on the effects of subdivision and twinning (Chapter IX).

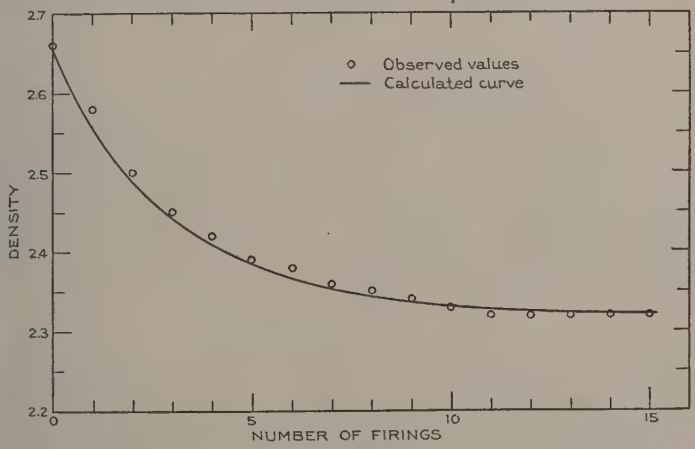


FIG. V.1.—Rate of transformation of quartz into cristobalite (Mellor & Campbell).

The rate of transformation of quartz into cristobalite is also very dependent on the temperature. The lowest temperature at which any change has even been suspected is 900°, and this only on powdered twinned pegmatitic quartz, the state in which it transforms the most rapidly. The transformation-rate becomes appreciable only above 1000°. The rate does not become relatively rapid until temperatures near or within the true cristobalite range are attained, although there is no evidence of any sudden increase at 1470°, the inversion point. At 1600° the transformation is usually complete within an hour.

Experimental data on the effect of temperature on the speed

Mellor & Campbell [17] have studied the speed of conversion of quartz into cristobalite by making 15 successive burns in a china biscuit kiln to cone 10

[17] MELLOR, J. W., & CAMPBELL, A. J., *Studies on flint and quartz (I)*, Trans. Engl. Ceram. Soc. (1915) **15**, 77-85.

(nominally 1330°), and measuring the density of the product after each burn. If the specific volume is additive the relative proportions of quartz and cristobalite can be inferred from the density.

The authors show that the relation of density to time (number of burns) is approximately that which would be predicted if the speed of conversion is proportional to the fraction which remains unchanged at any moment.

$$x = e^{-KZ}$$

in which x is the fraction which remains unchanged at the time Z, and K is a constant.

In Figure V.1 the observations of density are compared with the calculated curve

$$d = \frac{18.096}{7.8 - e^{-0.314N}}$$

in which N is the number of burns. This curve is based on the formula for x given above, assuming an initial density of 2.66 and a final density of 2.32.

There are numerous scattered observations on the rate of transformation of quartz to cristobalite at various temperatures, but they are not altogether consistent, probably because the large effect of state of subdivision and twinning was not recognized. These observations will now be reviewed, approximately in the increasing order of temperatures.

1000° and below

The only evidence of a change found by Endell & Rieke[18] in twinned pegmatite quartz heated for 48 hours at 900° was a slight decrease in density, hardly more than the error of measurement. It cannot be taken as proved, therefore, that any change whatever takes place in quartz under the conditions named. The temperature of 900° may even be below the metastable inversion-temperature of quartz to cristobalite.

Clews & Thompson[19] observed the following changes in density in powdered quartz heated at 1000° ± 20°, in a platinum crucible, in a nichrome-wound vitreous silica tube:

Period of heating	Density
0	2.634 at 9.2°
25 ¼ hr.	2.623 at 14.4°
48 ¾ hr.	2.627 at 9.8°
129 ¼ hr.	2.623 at 13.7°

If the diminution of density was due entirely to the formation of cristobalite, the total change noted above would represent the conversion of about 3 per cent of the quartz. But as no examination was made of the product, it is possible that most, or even all, of the change is due simply to the breaking up

[18] Endell, K., & Rieke, R., *Über die Umwandlungen des Kieselsäureanhydrids bei höheren Temperaturen*, Zeitschr. anorg. Chem. (1912) **79**: 239-259.

[19] Article cited in note [7].

of the quartz by the heating and cooling (see p. 144). In an earlier series, made at about 1030° by the same authors,[20] a specimen of the same quartz decreased in density from 2.631 to 2.571 after 109 hours heating. So large a change (one-fifth of the difference between quartz and cristobalite) is difficult to account for by cracking alone, and some cristobalite may have formed. The quartz used was massive vein quartz from Isle of Man, untwinned, but showing evidence of considerable mechanical deformation.[20] The mechanical effects would accelerate both the cracking and the inversion to cristobalite (see p. 136).

The initial density seems abnormally low, suggesting the presence of chalcedonic or hydrated silica, which invert much more rapidly than quartz (see XI).

Approximate range 1000 to 1300°

Berdel[21] heated Norwegian quartz in a gas furnace to temperatures of about 1000 to 1450° (cones 09 to 15). Only a small decrease in density was noted after heating to 1000-1250° (down to 2.63). At 1200-1450° a greater decrease occurred (down to 2.60-2.59).

Day & Shepherd[22] report fairly complete conversion of quartz into cristobalite after 6 days at 1160°. (The product was erroneously called "tridymite" in their first publication.) At the slightly higher temperature of 1200° the transformation took 3 days.

Fenner, on the other hand, found that at 1250° only a small percentage of his powdered quartz was transformed after 108 hours (about 4 days).

Houldsworth & Cobb[23] heated massive Meanwood ganister, a natural quartzite containing 97.2 per cent SiO_2, 6 times in a kiln to 1170°, the total duration of each burn being 72 hours. The density decreased from 2.65 to 2.59, which would correspond to 17 per cent cristobalite if due entirely to the inversion, but the amount of cristobalite actually formed was much less than this as shown by the dilatation curve of the specimen and its refractive index when powdered.

Conversion of grains of quartz, of varying sizes up to 3 mm diameter, in the clay of retorts used for the reduction of zinc, has been observed by Schulze & Stelzner.[24] These retorts had been held for four to six weeks at temperatures of 1200° to 1300°C. The grains of quartz were bordered by a zone 0.01 to 0.02 mm broad, faintly birefringent and showing indications of radial fibrous structure. The conversion product was considered by the authors to be tridymite, which was then the only crystalline form known in addition to quartz; but, to judge from the description, it was probably cristobalite.

Robson[25] compared the effects of high temperatures on two kinds of quartz: (1) pulverized quartz sand ("common potters' flint"), of which 93 per

[20] Correspondence with Messrs. Clews and Thompson.

[21] Berdel, E., *Feldspat und Quarz in niedrig gebrannten Massen,* Sprechsaal (1904) **37**: pp. 109-111.

[22] Article cited in IV, note [4].

[23] Houldsworth, H. S., & Cobb, J. W., *The reversible thermal expansion of silica,* Trans. Engl. Ceram. Soc. (1922) **21**: 227-276.

[24] Schulze & Stelzner, p. 145 of article cited in IV, note [21].

[25] Robson, J. T., *The influence of heat on the microscopic properties of silica in its different mineral forms,* J. Amer. Ceram. Soc. (1922) **5**: 670-674.

cent passed through a 300-mesh sieve; (2) "rock quartz," a pulverized sugar quartzite, previously calcined at 1000°C, of which 11 per cent remained on 200-mesh sieve and 23 per cent remained on a 300-mesh. Neither showed an change in refractive index after being heated up to cone 13 (1390°) durin 4½ hours. A similar heating to cone 14 (1410°) in 4¼ hours lowered th index from that of quartz to 1.509 for the fine powder, and 1.517 for th coarser rock quartz powder. (These are evidently average indices of an int mate mixture of quartz and cristobalite.)

Specimens of the same materials heated to 1430° by Rieke [26] showed th following changes in specific gravity:

	Original	Heated to 1430°
Pulverized sand	2.67	2.49
Rock quartz	2.66	2.49

These data of Robson and of Rieke as a whole indicate the beginning c fairly rapid conversion to cristobalite at about 1400°, with possibly a sligh difference in rate in favor of the finer powder.

Approximate range 1300 to 1500°

Fenner [27] found that the conversion of powdered quartz in the dry state wa about two-thirds complete after 90 hours at 1360°.

A further heating of Houldsworth & Cobb's material, already referred t amounting to 2 hours at 1410°, produced only a small additional amount c cristobalite over the amount formed at 1170°.

Schwarz [28] found that powdered quartz heated about 24 hours in a porcelai kiln, maximum temperature 1450°, decreased in density to 2.63. Four burn totaling about 100 hours, at the same temperature lowered the density to 2.5. This is roughly equivalent to about half conversion.

Parravano & Rosselli del Turco [29] found that a natural quartzite, mixe with 1.5 per cent of CaO in the usual process for making silica brick, was onl partly converted into cristobalite after being fired for 12 hours, with the tem perature rising to 1430°.

1500° and higher

At 1500° the transformation is about 85 per cent complete after 4 hours.[30]

Houldsworth & Cobb's material, already referred to, when heated furthe for 2 hours at 1530° to 1555°, appeared from the dilatation curve to have bee entirely converted to cristobalite, with indications from the refractive inde that a part had been further changed into tridymite.

At 1570° the conversion is practically complete within one hour accordin

[26] RIEKE, R., *"Quartz" und "flint" in Amerika,* Ber. Deutsch. Keram. Ges. (1921 2: 168-169.
[27] FENNER, articles cited in IV.
[28] Article cited in IV, note [20].
[29] Article cited.
[30] ENDELL & RIEKE, article cited in note [18].

to both Fenner and Braesco.[31] Mellor & Campbell[32] state that 3 hours at cone 35 (nominally 1755°) transformed about 65 per cent of their quartz.

General conclusion

Taken as a whole, the foregoing observations indicate the usual logarithmic increase in speed of a chemical reaction with temperature, the frequent discrepancies being probably due in most instances to differences in the state of twinning or the fineness of subdivision of the particular specimen used. It is also likely, however, that different admixtures have different accelerating effects on the transformation. (See, further, p. 78.)

The relative rates of conversion of various kinds and grain-sizes of quartzitic silica into cristobalite and tridymite are of great importance in the manufacture of silica brick. There are on record, accordingly, a number of investigations of the rate of conversion of natural quartz rocks of various types and different geographic sources. These investigations are an important source of knowledge concerning the phenomena and rates of transformation of the forms of silica, provided that the rocks themselves have been studied as to their composition and constitution. In most cases this has not been done, and the results are then of value only as bearing on the adaptability of a particular raw material to a particular process.

Historical notes on the transformation of quartz to cristobalite

The fact that quartz is changed by heating at a bright red heat into a fine-grained, chalky white product, was known for many years before cristobalite was recognized as a distinct form. The earliest record of this transformation that I know of was made by H. Rose[33] in 1859. By heating powdered clear quartz, of density 2.65, in a porcelain kiln to the highest temperature of the kiln (perhaps 1500°C) he succeeded in changing it into a form of much lower density, namely, about 2.33.

H. Rose also determined the specific gravity of fragments of silica, originally quartz, which he carefully separated out of a specimen of granitite (from Warmbrunn, Silesia) which his brother G. Rose had heated to the maximum temperature of the porcelain kiln. The resulting silica had a specific gravity, in the mass, of 2.337, and in fine powder, of 2.352.

Elsner,[34] in 1866, noted that clear fragments of quartz heated in a porcelain kiln (temperature probably about 1450-1500°) became cloudy or milky white, but he made no significant observations on the change.

H. Rose wrongly interpreted these changes as being due to conversion of

[31] Braesco, P., article cited in IV, note [14].
[32] Article cited in note [27].
[33] Article cited in IV, note [12].
[34] Elsner, L., *Ueber das Verhalten einiger Mineralien und Gebirgsarten bei sehr hoher Temperatur,* Journ. prakt. Chem. (1866) 99: 262-268.

the quartz into a so-called "amorphous" silica. Ten years later, in 1869, G. Rose [35] corrected this to the extent of showing that the product was crystalline, but assumed that it was tridymite. We know now that it was, in all probability, cristobalite.

Although the assumption that quartz is converted into amorphous silica by heating was shown by G. Rose in 1869 to be probably in error, the opinion was repeated in later works; for instance by Türreschmiedt [36] in 1870, and even by Bourry [37] in his standard treatise (1897); this, long after the product had been definitely shown to be crystalline, although it had not yet been certainly identified as cristobalite.

Aron [38] recognized in 1875 that quartz increases in external volume after being heated to dull red or higher. This was shown both by measurement of a single piece of quartz and by measurements of the dimensions of test pieces made of clay mixed with quartz sand, and having from 10 up to 350 parts of sand to 100 of clay. Such pieces expanded on burning when the proportion of sand was 50 per cent or more. Aron apparently did not recognize that the increase in the over-all volume of the quartz grains is greater than the increase in their true specific volume.

The direct transformation of quartz into cristobalite by heating was probably among the phenomena observed by Herschkowitsch [39] (1903) during his experiments on the fusion of quartz, although he supposed that the production of the white "porcelain-like material" was always the result of devitrification of the *glass*. The product had a specific gravity of 2.33, practically that of cristobalite.

Permutation (3): Cristobalite to tridymite

Temperature ranges

In the presence of a flux such as sodium tungstate, *below 870°*, cristobalite slowly recrystallizes to form tridymite, which then, being an unstable form in this range, proceeds further to change into quartz.

Being possible with a flux, this transformation is also logically possible in the dry state, but there are no observations on record to show whether or not cristobalite can be converted into tridymite by long-continued heating in the dry state below 870°.

Between 870° and 1470° tridymite is stable, and cristobalite, whether alone or in contact with a melt, inverts directly to tridymite as the stable form.

The speed of inversion of cristobalite to tridymite is slow, like that

[35] Rose, Gustav, article cited in IV, note [28].

[36] Türreschmiedt, A., Notizblatt Deutsch. Ver. Fabrication Ziegeln, etc. (1870) **6**: 206-209.

[37] Bourry, E., *Traité des industries céramiques* (1897, Paris). The error has been repeated in Searles' revised translation (Bourry, *A treatise on ceramic industries* (1911, London)).

[38] Aron, J., Notizbl. Deutsch. Ver. Fabrication Ziegeln (1874) **10**: 131-159; Dingler's Polytechn. Journ. (1875) **216**: 258-268, 438-445.

[39] Herschkowitsch, M., Zeitschr. physik. Chem. (1903) **46**: 408-414.

of the other inversions between the principal forms. At a given temperature it is much slower than the inversion of quartz to cristobalite.

The speed is apparently less at a temperature near the inversion point than at a temperature some distance lower. 5 hours' heating with sodium tungstate at 1460° produces only a small amount of tridymite, while 5 hours under similar conditions at 1380-1400° converts the cristobalite almost entirely into tridymite.[40] This relation of temperature and speed is rather unusual and deserves further examination.

TABLE V.1.

CHANGE IN THE CONSTITUTION OF SILICA BRICK ON REPEATED BURNING TO CONES 14-15 (NOMINALLY 1410-1430° C). (McDOWELL, PER ROSS.)

No. of burn	Percentage by volume		
	Quartz and silicates	Cristobalite	Tridymite
1	25	71	4
3	14	64	20
4	12	58	30
6	14	42	44
8	14	33	53
10	11	28	61

Experimental data

The relative slowness of the inversion of cristobalite to tridymite at a given temperature, as compared with the inversion quartz to cristobalite, is shown qualitatively by Endell's experiments.[41] Quartzite was converted almost completely into cristobalite by 5 heatings in a porcelain kiln (maximum 1450°). At the end of 10 heatings, the material was still mostly cristobalite, with wedges of tridymite just beginning to appear.

The same relation is shown in the growth of tridymite at the expense of cristobalite and quartz on continued heating of silica brick below 1470°, as may be seen from the data[42] in Table V.1. The table gives the results of microscopic estimates of the constituents of commercial silica brick made of Medina quartzite of the "regular grind," with 2.0 per cent of CaO. The natural impurities were about 1.7 per cent. Quartz is low after the first burn, though the remainder disappears much more slowly than the first portion. Tridymite steadily increases and cristobalite decreases through the entire series including the tenth burn. The ultimate result would evidently be about 87 tridymite, 13 silicates, no quartz, and no cristobalite.

Houldsworth & Cobb[43] studied the further changes caused by heat in

[40] FENNER, C. N., p. 123 of article cited in IV, note [18].

[41] ENDELL, K., *Ueber Silikaquarzite,* Stahl u. Eisen (1913) **33**: 1770-1775, 1855-1860.

[42] McDOWELL, J. S., quoted and supplemented by Ross, D. W., *Silica refractories,* U. S. Bur. Standards Techn. Paper **116** (1919).

[43] Article cited in note [23].

cristobalite which had been produced from precipitated micro-amorphous silica by heating for 2 hours at 790°. When this material was heated five times in a works kiln to cone 9 (maximum temperature 1170° by thermocouple), the product had a refractive index partly greater and partly less than 1.481; a density of 2.28; and an expansion curve beginning with a large expansion from 100 to 170° followed by a fairly large but regular expansion to 550° and a contraction to 1000°, the curve being repeated in the opposite sense on cooling.

Further heating for 2 hours to cone 14-15 (nominally 1410-1430°) caused no decided change in expansion or refractive index. The product was judged from the above-described properties to be at least half tridymite.

The rate is undoubtedly influenced by the presence of small amounts of other substances. Whether these act only by forming a liquid silicate or whether they have other more specific effects is not known.

Parravano & Rosselli del Turco's [44] quartzite mixture containing 1.5 per cent CaO was more influenced in its transformations by additions of B_2O_3 than by any other substance. Relatively large wedge-shaped twins of tridymite were formed within the mass of cristobalite which filled the spaces between unaltered quartzite fragments.

Phenomena of the inversion

Holmquist [45] observed that in the course of the transformation of quartz into tridymite by way of cristobalite any given fragment always went completely to cristobalite before any tridymite appeared. Fragments could be found in which residual quartz was mixed with cristobalite, and others in which new tridymite was mixed with cristobalite, but none in which all three were present. As it is difficult to conceive of any influence which could be exerted by a quartz fragment upon a surrounding mass of cristobalite crystals to prevent tridymite crystals from developing in the mass, the observation can be interpreted only to mean that cristobalite, after having formed from quartz, must lie an appreciable length of time at a high temperature before visible tridymite can develop from it.

This interpretation is strengthened by Holmquist's observation that when tridymite does begin to form in the cristobalite mass, it begins in many cases at the outside border of the original fragment and grows inward; that is, it begins where the inversion from quartz to cristobalite first began, and hence where the oldest cristobalite in the fragment is situated.

Le Chatelier [46] has reported the transformation of original well-formed cristobalite crystals into tridymite of much finer texture, the fragment retaining the original crystalline outline but consisting of very small tridymite crystals arranged in no visible regular relation to the parent cristobalite. The observation was made on silica brick from the crown of a glass furnace. The temperature at which the transformation occurred is not known, nor is optical evidence of the identification given.

[44] Article cited.
[45] Article cited.
[46] Le Chatelier, H., *Sur la cristobalite,* Compt. rend. Acad. Paris (1916) **163**: 948-954; Bull. Soc. Franc. Mineral. (1917) **40**: 44-57.

Sokolov,[47] also, has followed the transformation of quartz into tridymite in silica brick, by examining thin-sections of brick from the walls of steel furnaces. The grains of quartz begin changing at their outside surfaces to an isotropic material, and at the same time begin to break up into smaller and smaller particles. They ultimately become entirely isotropic, then faintly birefringent, then transform into an aggregate of new crystals of tridymite.

Permutation (4): Tridymite to cristobalite

Tridymite is an unstable form in the range of temperature from zero to 870° and again from 1470° to its melting-point. Its conversion into cristobalite therefore appears possible within both of these ranges, although below 870° further conversion of the cristobalite into quartz would be expected.

Below 870°, although logically possible, this transformation of tridymite into cristobalite as an intermediate phase has not been observed. Heat alone is without effect; while in the presence of a flux such as sodium tungstate, quartz, the stable phase, is formed directly.

Above 1470° tridymite, whether alone or in presence of a flux, inverts directly to cristobalite.

Speed of the transformation

The speed of transformation of tridymite to cristobalite increases rapidly with the temperature. At 1480°, only 10° above the inversion point, the transformation is about two-thirds completed after 15 hours heating in contact with sodium tungstate, while heating with tungstate at 1520-1540° completes the change within 4 hours.

The rate is notably slower in the absence of any flux. The transformation is about three-fourths completed after 7 hours at 1540-1560°, while at 1585° it is complete within 2 hours.[48] At 1650° pure tridymite remains unaffected by 10 minutes' heating.[49]

Le Chatelier[50] states that he has heated tridymite (from silica brick) for 2 hours at 1700° without producing any visible change. The temperature could hardly have been as high as 1700°, since the metastable melting-point of tridymite is at 1670°. But even at 1670° or slightly lower some change to cristobalite was to have been expected, unless possibly the rather large and well-developed tridymite employed by Le Chatelier had an appreciably slower rate of transformation. No optical evidence is cited, so it also remains possible that cristobalite was in fact present but was not recognized.

[47] Article cited in VI, note [25].
[48] Fenner, articles cited in IV, note [2].
[49] Endell, K., article cited in note [41].
[50] Article cited in note [46].

Permutation (5): Tridymite to quartz

Temperature ranges

Below 870° quartz is the stable form of silica, and tridymite should be convertible into quartz at all temperatures below 870°. This transformation has been repeatedly observed, but never as a result of heating tridymite alone. It occurs only in contact with a melt such as sodium tungstate (melting-point 700°), or in contact with a water solution sealed up in a bomb so that it can be heated above 100°.

From 870° to 1470° tridymite is stable, and can not be converted into any other crystalline form of silica if under conditions of constant and uniform temperature and pressure.

Above 1470° the inversion of tridymite to quartz as an unstable phase intermediate between tridymite and cristobalite, though logically possible, has never been observed.

We have to consider, then, only the range of temperature below 870°.

Phenomena of the inversion

There is no experimental evidence as to whether the change of tridymite to quartz in presence of a flux takes place only by way of intermediate solution, or whether it may also be produced by atomic rearrangement. Natural pseudomorphs of quartz after tridymite are known (see XLII) but have probably been produced by replacement.

Speed of the inversion

The speed of inversion of tridymite into quartz is notably slower than the reverse inversion of quartz into tridymite (observed at a temperature only slightly higher), and is far slower than that of vitreous silica into tridymite.

The experimental data

The transformation of tridymite to quartz has been studied by Day & Shepherd and by Fenner. The results have already been referred to in the discussion of the ranges of stability of the forms (see IV).

Fenner[51] has converted tridymite into quartz by heating it with molten sodium tungstate at 750° and 800°; also by heating tridymite with water and sodium carbonate in a silver-lined steel bomb.

At 860°, in the presence of sodium tungstate, only a small fraction of the tridymite exposed is converted at the end of 74 hours (3 days) heating.[51] At 750°, in the presence of a melt consisting of 80 per cent KCl and 20 per cent LiCl, quartz in quantity sufficient for positive identification appears after 5 to 6 days.[52]

[51] Articles cited in IV.

[52] Day, A. L., & Shepherd, E. S., article cited in IV, note [4].

Permutation (6): Cristobalite to quartz

Temperature ranges

Cristobalite is an unstable phase at all temperatures below 1470° and should therefore transform into a more stable modification if given the opportunity.

Below 870°, where quartz is stable, the inversion has been performed by heating cristobalite with water and Na_2CO_3 in a silver-lined steel bomb at 400-500°, crystalline quartz resulting (Fenner). But with cristobalite in the pure dry state there is no completely authenticated case of its conversion into quartz. The transformation should be readily possible with a molten flux, but under these conditions tridymite has always been found as the first product, an example of principle (2) (see p. 60), quartz forming only as a later product.

The conversion of cristobalite to quartz as an unstable phase *above 870°*, though logically possible, and even predictable under "Ostwald's Rule," has never been observed.

Speed of the inversion

The speed of inversion of cristobalite to quartz, passing through tridymite as an intermediate phase, is slow, like that of the other sluggish inversions. Finely powdered cristobalite heated with sodium tungstate at about 850° is completely converted into quartz (*via* tridymite) in 5 hours (Fenner).

Wietzel [53] claims to have produced quartz from artificial fine-grained cristobalite by 6 hours' heating at 600° C. The evidence is based solely on the heat of solution in hydrofluoric acid of a single sample, with no optical confirmation, and hence can not be accepted without further experiments. The evidence is good as far as it goes, however. 0.7 gram of finely ground and "slimed" cristobalite, made originally by heating Kahlbaum's precipitated silica for 68 hours at 1100°C, was dried in a platinum crucible and heated, with repeated stirring, for 6 hours at 600°. Its heat of solution in fuming HF was 36.55 kilogram-calories per 60.3 grams, as compared with 38.83 for vitreous silica. The difference in heat content from the glass is thus 2.28. The corresponding difference for quartz is 2.33, while that for cristobalite is only 0.57. Evidently the material which went into solution was much nearer to quartz than to cristobalite.

Wietzel suggests that the platinum acted as catalyst for the inversion. A more likely possibility is that the finely ground and suspended cristobalite was already in course of crystallization to quartz because of the presence of the water, and the process was very nearly completed during the time when the wet mass was being heated up to a temperature where the water was driven off completely.

[53] Article cited in note [13].

Acceleration of the transformations by other substances

The sluggish inversions of silica, particularly at temperatures above 1100°, are appreciably hastened by impurities in the silica. Their effect is especially noticeable if they are finely divided and uniformly distributed.

The effect of impurities in hastening inversions is probably due mainly to the formation of small quantities of liquid silicates which act like the sodium tungstate "flux" in the laboratory experiments already described. Their effect becomes noticeable, therefore, only at temperatures where such liquid silicates can form by interaction between the oxides SiO_2, Al_2O_3, Fe_2O_3, MgO, CaO, etc.

There may be other more specific effects. For example, boron trioxide, B_2O_3, is found to be much more active in accelerating the transformation of quartz than is CaO, Fe_2O_3, or P_2O_5. But so little is known of the fundamental facts upon which this acceleration depends that no general statements can be made beyond what has just been given. This subject might prove a profitable one for industrial research, since the transformations of silica are of great importance in the manufacture of silica brick and changes in speed or in the texture of the resulting products may lead to important changes in methods.

The importance of the impurities in hastening the inversions which are essential in the manufacture of silica brick was first pointed out by Grum-Grzimailo[54] in 1911.

Endell[55] observed that specimens of vein quartz as well as quartz from lenses or bands in gneiss ("Bandquarz") from Zillertal (Austrian Tirol) are readily converted into cristobalite by heating. The quartz specimens were not well developed crystallographically and many were twinned. The twinning undoubtedly hastened the inversion (see IX), but in Endell's opinion it may also have been accelerated by the gas and liquid inclusions which were abundant in these specimens.

The effect of impurities on the rate of formation of tridymite is qualitatively shown by the observation of Endell,[56] that the inversion of cristobalite to tridymite in a silica brick heated to 1450° took place most abundantly in the parts where the impurities were most abundant.

Another recent observation of this kind is that of Rebuffat,[57] who found that the quartzite of Lagonegro, Italy, of density 2.65, was transformed to silica of lower density (2.25) by heating for 8 hours at 1300-1350°. Analysis showed a sulfate residue (left after treatment with HF and H_2SO_4) of 5.50 per cent, of which 0.31 per cent was P_2O_5, with a notable amount of Fe_2O_3 and smaller quantities of other substances. After being treated with nitric acid the quartzite had a density of 2.60, which it retained after 8 hours' heat-

[54] Grum-Grzimailo, W., *Die Feuerfestigkeit der Dinassteine*, Stahl u. Eisen (1911) **31**: 224-226, pl. 6.

[55] Endell & Rieke, p. 253 of article cited in note [18].

[56] Endell, K., article cited in note [51].

[57] Rebuffat, O., *Sulla trasformazione del quarzo in tridimite*, Giorn. chim. ind. applicata (1920) **2**: 437-438; Trans. Engl. Ceram. Soc. (1921) **21**: 66-68.

ing at 1300-1350°. The extraction of the P_2O_5 by the acid seemed to be the cause of the loss of the property of transforming rapidly.

To test this, another fairly pure quartzite, which had a density of 2.60 and a sulfate residue of 0.62 per cent, and which remained unchanged by heating 8 hours at 1300-1350°, was mixed with 3 per cent of a glass containing 16 per cent P_2O_5, the percentage of P_2O_5 in the mixture as a whole being 0.45. The usual 8-hour heating now lowered the density to 2.22-2.27.

It was not the mere presence of P_2O_5 in Rebuffat's specimen, however, that was responsible for the acceleration of the transformation, because Parravano & Rosselli del Turco[58] obtained no such effect by the addition of 1.5 per cent of P_2O_5 in the form of calcium phosphate. It seems rather that the presence of a fluid silicate-phosphate mixture capable of dissolving and recrystallizing silica is the essential factor.

Parravano & Rosselli del Turco[59] made a series of experiments on the effect of small amounts of oxides added to a natural quartzite, in accelerating the conversion to tridymite and cristobalite. This quartzite (from Grignasco) has the following average composition: SiO_2, 96.5; Al_2O_3, 2.06; CaO, 0.80; Fe_2O_3, trace; loss on ignition 0.70. Test pieces were made following the usual processes for the manufacture of silica brick, with 1.5 per cent CaO, but with 0.5 to 1.5 per cent of other oxides in addition. The density was determined with a pyknometer, on the finely powdered specimen, using benzene as immersion liquid. The results are shown in Table V.2.

The addition of Fe_2O_3, P_2O_5, or CaO evidently has no noticeable effect on the speed of transformation, while B_2O_3 has a very considerable accelerating effect.

The conversion, as far as can be told from the density, seems to be complete in every case after the second burn, either with or without the additions.

TABLE V.2.

DENSITY OF QUARTZITE AFTER BEING HEATED WITH VARIOUS OXIDES. (PARRAVANO & ROSELLI DEL TURCO.)

	First heating. Fired 12 days. Max. 1430°C	Second heating. Fired 15 days. Max. 1490°C
Normal quartzite mix	2.50	2.31
Same + 1.5% Fe_2O_3	2.48	2.32
Same + 1.5% P_2O_5	2.51	2.31
Same + 1.5% CaO	2.51	2.32
Same + 0.5% B_2O_3	2.43	...
Same + 1.0% B_2O_3	2.40	...
Same + 1.5% B_2O_3	2.42	2.32

RELATION BETWEEN STABILITY AND REACTIVITY

Since the relative stability of the different phases or polymorphous modifications of a substance may be expressed in different escaping tend-

[58] Article cited in note [8].
[59] Article cited in note [8].

encies or fugacities,[60] their reactivities or rates of solution and reacti with other substances may also be expected to differ. Other conditio being the same, an unstable form should react or dissolve more rapic than the stable form.

A relation of this kind has been observed in the rate of reaction of sili with molten sodium chloride and moist air to form sodium silicate and hydr chloric acid. Clews & Thompson[61] observed the following production of H from 50 per cent mixtures of SiO_2 and NaCl, heated 6 hours in moist air 1003°, rate of air-flow 88 cc per hour through tubes 9 to 10 mm in diamete

Quartz	.....	50.5 cc	of	N/100 HCl
Precipitated silica	.....	42.0 cc	"	" "
Tridymite	.....	38.8 cc	"	" "

Since precipitated silica is readily converted into tridymite at 1000° in a flu its rate of reaction should be near that of pure tridymite. Quartz, on th other hand, being unstable at 1000° yet not rapidly convertible into tridymit should be more reactive, as is found to be the case.

Schwarz[62] has made the most careful comparative measurements that w have on the dissolving-rate of quartz, tridymite, cristobalite, and vitreou silica. He used samples of uniform granularity, about 0.04 mm size, obtaine by fractionating the powders in a Schöne's sliming apparatus, using the por tion between the speeds of 0.2 and 1.5 mm per second. Quartz and tridymit were compared by boiling in 5 per cent Na_2CO_3 solution for one-half hour The dissolving-rates of all four forms in HF solutions were compared by heating 1 gram in 100 cc on a water-bath for 30 minutes or 1 hour, with con stant stirring. The results are given in Table V.3.

TABLE V.3.

DISSOLVING-RATES OF THE FORMS OF SILICA. (SCHWARZ.)

Percentages dissolved.

	5 per cent Na_2CO_3 ½ hour	5 per cent HF ½ hour	1 per cent HF 1 hour
Quartz	2.11	30.1	5.2
Tridymite	2.77	76.3	20.3
Cristobalite	...	74.3	25.8
Vitreous silica	...	96.6	52.9

Historical notes on dissolving-rates

Experiments on the dissolving-rate of several forms of silica were made by Winkler[63] in 1878. The specimens which contained water were first heated to a bright red. About 30 mg of finely powdered silica was taken for each

[60] LEWIS & RANDALL, *Thermodynamics* (1923, New York), p. 190.
[61] Article cited in note [7].
[62] Article cited in IV, note [20].
[63] WINKLER, CL., *Die Untersuchung des Eisenmeteorits von Rittersgrün,* Abhandl. (Nova Acta) Kais. Leop.-Carol. Akad. Naturf. Halle (1878) **40**: 331-382, p. 358.

test, and was boiled in normal KOH solution for 1 hour in a flask with a long narrow neck which served to condense the steam and return it. The results are given in Table V.4.

TABLE V.4.

DISSOLVING-RATE OF SILICA IN NORMAL KOH SOLUTION AT BOILING POINT. WINKLER, 1878.

30 mg in 25 cc solution.

Form or variety	Source	Time	Per cent dissolved
Micro-amorphous, dehydrated ...	Made from water-glass	1 minute	100
Opal, dehydrated	Borsoe, Hungary	1 hour	89.1
Hyalite, dehydrated	Walsch, Bohemia	1 hour	56.1
Tridymite	Siebenbürgen	1 hour	49.6
Asmanite (tridymite)	Rittersgrün meteorite	1 hour	43.9
Micro-amorphous (or cristobalite?) dehydrated	Made from SiF_4 and H_2O	1 hour	23.4
Quartz			5.1

A similar contrast between micro-amorphous forms (see XI) and quartz was observed by H. Rose.[64]

PROPERTIES MOST USED IN IDENTIFYING THE THREE PRINCIPAL FORMS OF SILICA

In connection with this subject of the sluggish inversions of silica, some brief notes on the principal criteria used in distinguishing the forms will not be out of place, since correct conclusions regarding the transformations of the forms can be drawn only from correct identifications.

The ideal way to identify a substance is the way we use to identify our acquaintances,—simply look at them and recognize them by their shape and coloring. This simple method, with the aid of the microscope to sharpen our vision, sometimes serves perfectly well for the forms of silica.

Where long-continued heating has given opportunity for development of the crystals, as in a silica brick whose temperature has not fluctuated too widely, it is not difficult to distinguish cristobalite and tridymite simply by their appearance in the thin-section.

The tridymite crystals in a silica brick sometimes have opportunity to develop into characteristic plates and wedge-shaped twins, and can then be recognized at once. (See, for example, the photomicrographs by Rieke & Endell.[65])

Quartz is seldom found in well-developed crystals in such materials as rocks or refractory products, and hence is not identifiable simply by its shape.

[64] Article cited in IV, note [12].
[65] Article cited in note [14].

Density

The measurement of density has been often used in studying the transformation of quartz into cristobalite and tridymite, which have a much lower density than quartz. The measurement is usually made on finely powdered material in a pyknometer. For distinguishing cristobalite from tridymite it is unreliable, because these forms may have an apparently low density on account of fine pores, and cristobalite formed under some conditions may actually have a variable density. (See p. 302.)

Optical properties

The data upon which the petrologist depends fundamentally for his identifications are the numerical values of the indices of refraction together with the relations of the indices to one another and to the symmetry of the crystal. (See XXX.) With the petrographic microscope and suitable preparations of material it is easy to note the order of magnitude of the difference between two refractive indices, known as the "birefringence" or "double refraction." Quartz shows distinct double refraction, lighting up and darkening as the stage of the microscope is rotated with the nicol prisms in crossed position. Tridymite shows much less birefringence, cristobalite scarcely any, and vitreous or amorphous silica none.

It should be noted, however, that the phenomena as actually seen are strongly influenced by the chance orientation of the fragment, for a flat piece of any birefringent substance can be taken in one or more special positions in which it does not show the phenomena of double refraction at all, while in other positions it will show effects intermediate between zero and the maximum which is characteristic of the substance. The appearances are also influenced by twinning and by the overlapping of crystals in fine-grained material.

The actual values of the refractive indices can be measured to within 0.002, or even 0.001, on a minute quantity of powdered material, by the method of immersion in standardized index-liquids, described in most text-books of petrology.[66] These data, as well as other less used optical properties, are listed in Chapter XXX.

The indices of quartz are so much higher than those of the other forms as to leave no doubt of the identification. The indices of tridymite and cristobalite are not far apart, but sufficiently different to afford reliable identifications if the material is reasonably well crystallized.

With the very fine-grained and porous cristobalite which results from heating such materials as chalcedony or flint the optical methods fail

[66] See also WRIGHT, F. E., *The methods of petrographic-microscopic research*, Carnegie Inst. Washington, Publ. **158** (1911).

Such cristobalite may appear isotropic and indistinguishable from amorphous silica, and its apparent index may vary considerably.

Inversions, observed optically

In such a case the changes of properties at the high-low inversion of cristobalite are very valuable in identifying the substance,—are, in fact, essential when the material is so fine-grained that the optical properties can not be determined with certainty.

If the crystal fragments are large enough so that a slight birefringence is visible, then the sudden disappearance of birefringence at 220 to 280° C shows the material to be cristobalite.

If the material is being observed in the dry state, without immersion in index liquids or fixing in Canada balsam, the simple observation of transparency may be enough. Low-cristobalite is usually opaque, because the original crystal has separated into many smaller units in cooling through the inversion. But if the fragment has not been broken up mechanically, then the subdivided parts and the gaps between them will remain relatively undisturbed, and on reheating through the inversion point the gaps will close up and the fragment will again become transparent.

These optical observations at the inversion point are inconvenient, since they call for some kind of thermal microscope, or at least for some experimental arrangement by which the material may be heated on the microscope stage. Such apparatus is not available in most laboratories. Furthermore, if the cristobalite is so fine-grained as to be practically isotropic the optical observations are not conclusive.

The volume-change at the inversion, as determined with a dilatometer, is then very useful in identifying either cristobalite or tridymite.

Volume-changes at the inversions

The large volume-change in cristobalite at its inversion point (see VII and XX) makes this property a good criterion for distinguishing cristobalite from tridymite when in the form of a fine-grained aggregate. The density, refractive index, and rates of solution of the two are very nearly the same, but the volume-change on inversion is so much greater in cristobalite than in tridymite that it leaves no doubt as to which form is present. The temperature at which it occurs is also about 100° higher than for tridymite.

The method may be applied either by means of bars of the material tested [67] or by means of a dilatometer containing a liquid.[68]

[67] See, for example, Houldsworth & Cobb, article cited in note [23]; or Braesco, article cited in IV, note [24].

[68] See, for example, Washburn & Navias, J. Amer. Ceram. Soc. (1922) 5: 565-585.

Thermal curves

The dilatometer method is probably more dependable than the thermal-curve method in identifying cristobalite by its inversion-temperature, but the thermal-curve method may be more convenient if the apparatus is at hand. A distinct thermal effect can usually be found at 220 to 280° by means of a direct time-temperature curve made with a sensitive thermel such as a copper-constantan thermocouple.[69] It is brought out much more distinctly by a differential thermel such as is shown diagrammatically in

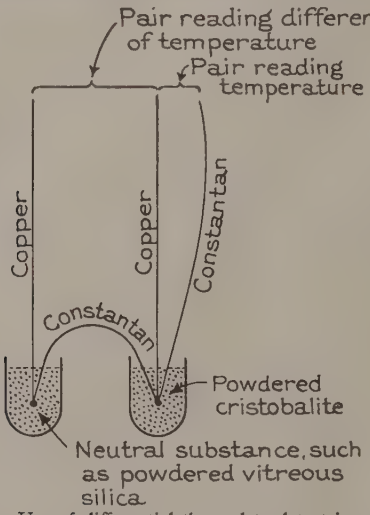


FIG. V.2.—Use of differential thermel to detect inversion points.

Figure V.2. The inversions of tridymite are not shown very distinctly by this method.

Comments on an actual case

An example of the quantitative application of both optical and expansion methods is found in the work of Houldsworth & Cobb.[70] The general statement may be made regarding their work that they have usually found more cristobalite and less tridymite in their silica than have other investigators. In distinguishing the forms they depended mainly upon the volume change at the inversion of cristobalite and upon the refractive indices of the forms. The first criterion, the volume change, is recognized now by all as an undeniable indication of the presence of cristobalite, but as to the quantitative interpretation of the amount of change observed there is still some uncertainty.

[69] See, for example, FENNER, articles cited in IV, note [9].
[70] HOULDSWORTH & COBB, article cited in note [23].

The criterion of refractive index, as used by Houldsworth & Cobb, is not so certain in its application as their statements would indicate. They used three oils, whose indices are related to those of the forms as shown below:

Oil	1.468
Tridymite	1.469 to 1.473
Oil	1.481
Cristobalite	1.484 to 1.487
Oil (cedar wood)	1.503
Quartz	1.544 and 1.553

There should be no difficulty about identifying quartz, with its high index. Cristobalite is more uncertain, because of its habit of occurrence in very fine-grained aggregates whose apparent density and apparent index are, in some preparations, abnormally low. Nevertheless, material clearly above 1.481 and below 1.503, which were the indices of Houldsworth & Cobb's oils, may be safely taken as cristobalite, so that the error, if any, would be in the direction of diminishing rather than increasing the apparent proportion of cristobalite. The change of index of the oils with temperature must be looked out for, since it may amount to several units in the third decimal place, but the index 1.481 could hardly be lowered by this cause by an amount sufficient to include much tridymite with the cristobalite.

The oil of index 1.468, however, is too close to tridymite. Especially if increased in index by cooling, this oil might cause much of the tridymite to be classed as some low-refracting silicate or other substance, although the birefringence which is nearly always distinctly evident in tridymite ought to prevent its being classed as silicate glass or as vitreous or amorphous silica.

With a better selected set of standardized index liquids, particularly liquids which will not change rapidly by evaporation, and with some experience in the examination of fine-grained substances, it should not be difficult to make an approximate estimate of the amounts of tridymite and cristobalite present.

Chapter VI. MELTING AND VAPORIZATION

In the preceding pages (see IV and V)* we have described the phenomena of the interconversion of the three principal crystalline forms of silica. There remain two other phases to be considered, namely, the liquid and the gaseous phases.

The liquid phase

At a temperature well above 1700° silica exists in the form of a liquid, which assumes a level surface when it comes to rest, and which flows under small stresses. When cooled, under conditions such that it does not crystallize, this liquid gradually stiffens until at room temperature it is what is called a *glass*. No sudden transition is observed from the liquid to the glassy form, hence liquid and glass are assumed to be but two aspects of a single phase, the *liquid-vitreous* phase, usually referred to in Phase-Rule discussion simply as the "liquid phase."

We have already considered the 6 possible permutations of the 3 crystalline phases, taken in pairs. The addition of a liquid-vitreous phase increases the permutations in pairs by 6, making a total of 12, the new ones being as follows:

(7) Cristobalite to liquid-vitreous
(8) Tridymite to liquid-vitreous
(9) Quartz to liquid-vitreous
(10) Liquid-vitreous to cristobalite
(11) Liquid-vitreous to tridymite
(12) Liquid-vitreous to quartz

These will now be considered in the order just given, the first three comprising the data on the fusion of the principal forms of silica, the second three comprising the data on the devitrification of vitreous silica.

The fusion of crystalline silica

Permutation (7). Cristobalite to liquid-vitreous. The melting-point of cristobalite

Cristobalite, the stable form of silica above 1470°, melts at 1710° ± 10°C. In common with quartz and tridymite, it shows the phenomenon of slow melting, as compared with ordinary salts and metals. Finely powdered cristobalite may be expected to melt completely to liquid, if held at 1715 to 1720°, in about 10 to 15 minutes.

* These text-references are to Chapters of this book. Any terms or abbreviations the meaning of which may be in doubt will be found defined in the Index.

The phenomena

The melting-point of a crystalline solid is the temperature at which crystal and liquid are in equilibrium with each other.

The true melting-point of high-cristobalite, the crystalline modification of silica which is stable at the highest temperature, is, under this definition, unusually difficult to determine. This difficulty is due to two factors: (A) the great viscosity of the liquid; (B) the slow time-rate of melting, a phenomenon which is comparatively rare and has made itself felt strongly only in the study of silica and the more siliceous silicates.

(A) High viscosity in the liquid has the result that the material does not flow when the crystal melts, and the fragments retain their original shape and position. Thus the melting is not immediately followed by visible evidence of liquidity.

(B) Slow rate of melting has the result that no appreciable heat absorption can be detected in a time-temperature curve, for it may be necessary to hold a charge for fifteen minutes or more at a given temperature before a noticeable amount of it is melted.

But the high viscosity and low rate of melting are accompanied also by an unusually small tendency to recrystallize on cooling, so that molten silica, and silicates high in silica, nearly always solidify to amorphous glasses, whereas metals and most salts crystallize readily as soon as these substances cool below their melting-points. This fact makes possible the "quenching" of silica and silicate mixtures from a given high temperature down to atmospheric temperatures, with no change in the relations between liquid and crystals which prevailed at the high temperature. Examination under the microscope then shows, by the presence or absence of amorphous glass, whether any of the substance was in the liquid state at the time it was quenched. This is the most reliable method for determining the melting temperatures of the forms of silica.

Experimental data on the melting-point of cristobalite

Using the method of quenching described above, Fenner[1] found that when cristobalite made from purified quartz was heated for 15 minutes within a magnesia tube in a carbon-tube furnace at 1680-1690°, an appreciable amount of glass was formed. Half an hour's heating at about 1645° produced a small amount of glass which could be plainly seen; at 1635° most of the grains were unaltered, but a few showed a little glass in minute ridges; at 1625° glass was believed to be present but there was some uncertainty. Fenner therefore placed the melting-point of cristobalite at 1625°C.

Endell & Rieke,[2] using a similar quenching method, found that cristobalite heated for 10 minutes at 1650° was unchanged; 10 minutes at 1675° caused the fusion of a portion around the borders of the charge; and 10 minutes at

[1] Fenner, C. N., article cited in IV, note [2].
[2] Endell & Rieke, article cited in V, note [18].

1700° caused complete fusion. They therefore placed the melting-point at 1685° ± 10°. The cristobalite used for these tests was made by heating powdered silica glass, and its composition is given as 99.9 per cent SiO_2. Similar results were obtained by them with cristobalite made from Norwegian pegmatite quartz and from Brazilian chalcedony.

Endell [3] made further experiments in 1913 on commercial quartzites and silica brick, which seemed to confirm the belief that the melting-point of cristobalite is in the neighborhood of 1685°. He found no megascopic indications of fusion in a specimen of cemented-quartzite after 10 minutes at 1650°, but observed rounding of edges at 1690°, and complete fusion at 1700°. Finely powdered pure Brazilian quartz, silica brick consisting chiefly of tridymite, and similar brick consisting chiefly of cristobalite, were also completely fused in 10 minutes at 1700°. A quartzite somewhat purer than the cemented-quartzite, and also some cristobalite made therefrom, were similarly tested and showed rounding of edges at 1710°.

These tests were made in an electrically heated iridium tube furnace, and the temperatures were measured with an iridium/iridium-ruthenium couple; estimated accuracy ± 10°.

Ferguson & Merwin [4] took up the question again in connection with their work on the ternary system SiO_2:MgO:CaO. Using cristobalite made from pure quartz and also from vitreous silica, they quenched the material from various temperatures between 1638° and 1737°, heating it in a "cascade" furnace of which the inner coil was of platinrhodium wire (20 per cent Rh) wound on magnesia. The results show definitely that the melting-point of high-cristobalite is about 1710°. Fenner's lower figure may have resulted from small amounts of impurity, either present in the silica, or, more probably, distilled into it from the carbon or the magnesia tube in which his tests were made.

Wietzel [5] measured the melting temperature of cristobalite in two ways: (1) About ½ gram was held at a constant temperature in a platinum crucible in an iridium tube furnace, and then quenched, the first appearance of glass on particles around the edges of the charge being noted; (2) quartz fragments were first heated at 1600° to produce a surface layer of cristobalite, and these fragments were then heated as above described and the temperature of disappearance of the surface skin and rounding of the sharp corners was noted. Temperatures were measured with a Wanner optical pyrometer. The melting-points, corrected to the scale used in this book, were 1690° by the first method and 1687°C by the second method. Wietzel [6] gives as his opinion that the melting temperature is 1700° ± 10°, with a probability that it is above rather than below 1700°.

[3] Endell, K., article cited in V, note [41].
[4] Ferguson, J. B., & Merwin, H. E., article cited in V, note [2].
[5] Wietzel, R., article cited in V, note [13].
[6] Correspondence with the author.

Permutation (8). Tridymite to liquid-vitreous. The melting-point of tridymite

The transformation of tridymite to cristobalite is so slow that it should be possible to heat tridymite above 1470°, its enantiotropic inversion temperature to cristobalite, and observe the melting of tridymite itself. The melting-point of tridymite, if realizable, would be expected to lie between the melting-points of quartz and cristobalite, that is, it should be lower than 1710° and higher than about 1500°.

This expectation is realized. Ferguson & Merwin[7] have shown that tridymite has a clearly defined melting-point at 1670° ± 10°. The rate of melting is slow, when compared with the melting of salts and metals. Small crystals of tridymite may be expected to melt completely to glass at 1675° to 1680° in about 20 minutes.

The experimental data on the melting of tridymite

Ferguson & Merwin's figure of 1670° for the melting-point of tridymite is in agreement with an observation by Endell[8] in 1913, that pure tridymite was completely fused at 1690°.

Le Chatelier[9] has published photographs of thin-sections of silica brick from an open-hearth steel furnace, showing primary tridymite in contact with vitreous silica, with no intermediate formation of cristobalite. This is entirely in accord with facts and principles presented in preceding pages of this book, and does not necessarily show, as stated by Le Chatelier, "that tridymite is stable up to its point of fusion."

Quensel,[10] in 1906, reported the melting-point of tridymite as 1560°. This was determined in a thermal microscope, where conditions were not favorable for exact temperature measurement, and need not be given much weight.

Permutation (9). Quartz to liquid-vitreous. The melting-point of quartz

On account of the very slow rate of transformation of quartz into one or the other of the more stable forms, it is possible to heat quartz above 870° (its enantiotropic inversion point into tridymite) and to get evidence of the melting of quartz itself. Being an unstable form in this temperature region, quartz may be expected to melt lower than cristobalite, and such is found to be the case. Its true melting-point is not accurately known, but is probably below 1470°.

This is *not* the temperature meant by the general expression "the melting-point of silica." That expression refers to the melting of the high-temperature stable form, cristobalite. (See p. 86.)

[7] Ferguson & Merwin, article cited.
[8] Endell, K., article cited in V, note [41].
[9] Le Chatelier, H., article cited in V, note [■].
[10] Quensel, P. D., article cited in IV, note [10].

The rate of melting of quartz is very slow; so slow, in fact, that it may be equalled or exceeded by the rate of crystallization of the resulting glass into cristobalite. Hence the difficulty of determining what is the real melting-point of quartz.

The direct fusion of quartz without the intermediate production of any other form of silica has been repeatedly observed, and at a great many different temperatures. In part, this variety in the temperatures is the result of inadequate apparatus or methods for the measurement of high temperatures, but mainly it is due to the slow rate of melting, which permits quartz to be considerably overheated if the temperature is rising rapidly. Visible appearances of flow may then follow at almost any temperature from 1500° up to 1750°, according to the rate of heating.

The experimental data

Fusion without the production of cristobalite

In 1902 Brun[11] melted a fragment of quartz held on a platinum support, and heated by radiation from the walls of an enclosure within a muffle, which in turn was heated by an oxy-gas flame. The temperature was estimated by means of Seger cones. Quartz was found to flow at a nominal temperature of 1780°, which, corrected to the scale used in this book, is equivalent to about 1750°. It did not flow appreciably until 1820° (corr.), and was unaffected, except by cracking, at 1300° to 1550°.

Hempel,[12] in 1903, gave the "softening point" of quartz as 1685°, determined in an electric arc furnace with a Holborn-Kurlbaum optical pyrometer. The point of softening was determined by the descent of a rod resting upon a flat fragment of quartz, which bridged an opening in a carbon container. The heating was relatively rapid. The method evidently is not one of high precision. Comparison with other melting-points determined in the same furnace indicates that the results are low.

Heraeus,[13] in the same year, placed the melting-point of quartz at 1700°, as determined on fragments of quartz with an iridium/iridium-ruthenium thermocouple in an iridium vessel heated with an oxy-hydrogen flame. The scale and basis of calibration are not stated but the melting-point of platinum is given as 1780°; corrected to the scale used in this book (Pt = 1755°), this would make his melting-point of quartz 1675°.

Lampen[14] (1906) observed rounding of edges of a fragment of quartz, heated in graphite in a carbon resistance furnace, at 1650°, and fusion at 1700°.

Stein[15] observed that quartz, heated in a crucible of compressed carbon in

[11] Brun, A., *Étude sur le point de fusion des minéraux,* etc., Arch. sci. phys. nat. (1902), (4), **13**: 352-374, pl. 2.

[12] Hempel, W., *Ueber Schmelzpunktsbestimmungen bei hohen Temperaturen,* Ber. Int. Kongress Angew. Chem. (1903) **1**: 715-725.

[13] Heraeus, W. C., *Ueber Quarzglas,* Ber. Int. Kongress Angew. Chem. (1903) **1**: 708-715; Zeitschr. Elektrochem. (1903) **9**: 847-850.

[14] Lampen, A., *An electrical resistance furnace,* etc., J. Amer. Chem. Soc. (1906) **28**: 846-853.

[15] Stein, G., *Über die Darstellung einiger Silicate,* Inaug. Diss. Göttingen (1907) 31 pp.; Zeitschr. anorg. Chem. (1907) **55**: 159-174.

an electric resistance furnace, could be made to flow under pressure of a carbon rod at 1600°, and flowed readily at 1750°. Temperatures were determined with a Wanner optical pyrometer.

Endell & Rieke[16] in 1912 observed that a fragment of quartz, after being partly melted by *rapid* heating, shows no trace of cristobalite, but only glass together with unchanged quartz. Such melting could be brought about at 1600° or higher (Rieke, quoted by Wietzel[17]).

Cusack[18] (1897) using very finely powdered quartz on the ribbon of a Joly meldometer, observed softening at 1456°, very viscous flow at 1475°, and at 1490° fluidity like that of water. (The temperatures are corrected to the scale used in this book by addition of 50°, since Cusack assumed 1500° as the melting-point of palladium.) Joly,[19] in his first description of the meldometer, gives a similar figure for the melting temperature (1480°, corrected).

By heating powdered quartz in an iridium-tube electrical resistance furnace Day & Shepherd[20] (1906) found that part of it melted directly to a viscous liquid or glass at all temperatures from 1755° down to 1650°. The specimens were heated for about 20 minutes at each temperature. At the same time part of the quartz was found changed to another form, supposed at the time to be tridymite, but shown subsequently to be cristobalite.

The highest melting temperature recorded is by Matignon[21] who observed the fusion of clear transparent crystals in an electrically-heated carbon-tube furnace, measuring the temperature with a Wanner optical pyrometer. Five determinations gave 2040° to 2050° as the melting temperature. Platinum melted at 1746° and the melting-point of alumina agreed with Ruff's determination (2020°). As the best present values for these two points are 1755° and 2050°, respectively, Matignon's temperature measurements seem reliable. The unusually high temperature of visible melting must then have been attained by the rapid heating of single crystals, or else the crystal lagged far behind the temperature of the carbon block beside it, upon which the optical temperature observations were made. So high a melting temperature can not be accepted without further confirmation.

The foregoing observations give evidence of the direct fusion of quartz to glass at various temperatures from 1456° to 1755°, and perhaps higher. The lowest temperatures (1456° to 1490°), reported by Joly and by Cusack, seem abnormally low in comparison with all the other data, but receive support from the later observations by Fenner. I consider that Joly's and Cusack's values may be uncertain by 50° or more, depending as they do upon the visible fusion of a minute particle of palladium as a standard, the palladium lying on a strip of platinum heated electrically. They do,

[16] Endell & Rieke, article cited in V, note [15].
[17] Wietzel, R., article cited in V, note [13].
[18] Cusack, R., *On the melting points of minerals,* Proc. Roy. Irish Acad. (1897) (3), **4**: 399-413.
[19] Joly, J., *On the determination of the melting points of minerals,* Proc. Roy. Irish Acad. (1891) (3), **2**: 38-64, pl. 6.
[20] Day & Shepherd, article cited in IV, note [4].
[21] Matignon, C., *Le point de fusion du quartz,* Compt. rend. Assoc. Franc. Av. Sci. (1911) **40**: 159.

however, support the general statement that quartz can be melted to glass at temperatures well below 1600°.

The low values obtained by Joly and by Cusack may possibly be due in part to the fact that the melting temperature of a substance is lowered by very fine subdivision (see XI), but it seems hardly likely that this lowering could be of the order of magnitude of 100°.

Qualitative data

In addition to the quantitative measurements already described, there are a number of qualitative observations on record of the fusion of quartz. Only brief mention need be made of the observations by Spezia,[22] who found that a simple blowpipe fed with air, or a Fletcher blowpipe fed with warm air, would not melt quartz, but that a Fletcher blowpipe fed with oxygen under 25 mm pressure melted it easily to a clear glass. Hyalite melted to a foamy glass.

Fusion with simultaneous production of cristobalite

In the foregoing observations no cristobalite or tridymite was observed, but only quartz and glass. It is not uncommon, however, to find cristobalite forming from the glass if fusion has occurred below 1710°. Day & Shepherd, in the experiments just cited, observed this transformation.

In connection with his study of the interrelations of the forms, Fenner [23] was interested in the preliminary melting of quartz as a step in its conversion to cristobalite above 1470°. He therefore made a series of experiments on the fusion of powdered quartz, and observed that quartz grains heated at 1530° for 30 minutes were bordered by a band of appreciable width, whose index was generally less than 1.475 and in some instances less than 1.465. Quartz grains heated for one hour at 1470° were likewise surrounded by a narrow border of lower, and variable, index. The low-refracting material also cut across many grains, leaving portions of some crystals detached, and causing an irregular pitting and corrosion of other crystals. The material was isotropic to faintly birefringent, and was probably a submicroscopic mixture of silica glass and cristobalite.

This intermediate melting was confirmed by an experiment of Ferguson & Merwin,[24] in which a large quartz crystal heated at 1691° for one hour, and then quenched, showed a core of unchanged quartz, surrounded by a zone of glass which in turn gave way to an outermost zone of homogeneous crystalline cristobalite.

A similar change of quartz into an isotropic phase, followed by development of faint birefringence (presumably cristobalite) and finally by the formation of tridymite, is described by Sokolov.[25]

[22] Spezia, G., *Sulla fusibilita dei minerali,* Atti R. Acc. Torino (1887) **22**: 419-426.

[23] Fenner, articles cited in IV, note [3].

[24] Ferguson & Merwin, article cited in V, note [3].

[25] Sokolov, V. I. (*On the transformation of quartz under the influence of high temperature*), (Russian), Proc. Imp. Mineral. Soc. St. Petersburg (1906) **44**: 473-482, pls. 8-9.

The melting-point data as a whole may be fairly summarized in the statement that the melting-point of quartz is probably below 1470°, but that at this temperature the rate of melting of the quartz and the rate of transformation of the resulting glass into cristobalite have become nearly the same. Below this temperature the glass changes to cristobalite as fast as formed, while above about 1500° the formation of glass is able to keep ahead of the crystallization to cristobalite. Above 1710° there is no tendency to crystallize. This interpretation is illustrated by the sketch in Figure VI.1.

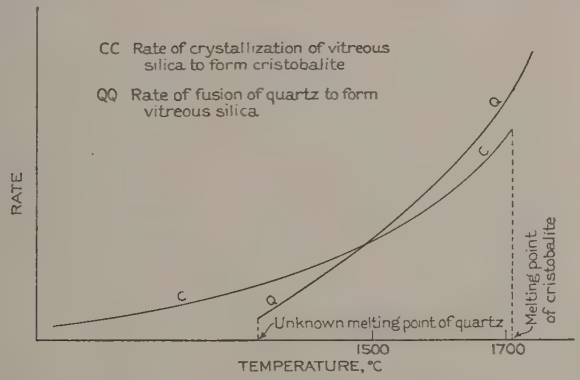


FIG. VI.1.—Imaginary curves to illustrate the fusion of quartz.

The non-appearance of cristobalite in Cusack's experiments is in agreement with the general observation that it is much easier to undercool very fine drops of a substance than large masses.

Other data on the fusion of quartz

We might still ask whether it may not be possible that quartz undergoes some change in structure before melting, even though tridymite or cristobalite do not appear. An experiment by Mügge[26] partly answers this question, showing that quartz has a distinct melting-point of its own and that rapid melting is not preceded by any sharply distinguished change in structure. He covered half of a quartz plate with sheet platinum, and melted the exposed half in an oxy-gas flame, obtaining thus a sharp division between glass and crystal. When again heated to the high-low inversion point this quartz behaved exactly like quartz which had never been previously heated, and gave similar etch-figures, up to the very boundary of the glass.

The experiment also indicates that if any temporary intermediate

[26] MÜGGE, O., Neues Jahrb. Min. etc. 1907, Festband, pp. 181-196.

phase is produced which is molecularly or even optically homogeneous and continuous with the quartz or glass, it must either have a very short life and occupy a very narrow zone between the two, or else be of the character of the "glass with crystalline properties" to be described in Chapter VIII. Brun [27] thought that he might have evidence of the existence of an intermediate molecularly homogeneous phase varying in structure from that of quartz to that of glass when he observed a progressive lowering of the index of refraction of quartz after repeated heatings to a temperature sufficient to cause fusion. The birefringence faded away similarly after a certain stage of fusion. These observations are most reasonably explained as due to very fine-grained or even submicroscopic mixture of quartz and glass, or perhaps of cristobalite and glass, the crystalline and glassy phases remaining distinct, but the increased proportion of glass at each heating causing a lowered average index. On the other hand, it would be a pure assumption to say that Brun's first explanation is not a possible one, even though Mügge's experiment is against it. Evidence in Chapter VIII will show that it is quite reasonable, and more experimental data will have to be obtained to settle the question.

Some specimens of vitreous silica contain very small inclusions of quartz. Rayleigh [28] has examined some of these, observing that the glass showed, in polarized light, bright crosses 1 to 2 mm in diameter, with birefringent grains 0.1 to 0.2 mm in diameter at the center. These centers were identified as quartz by Watts and Holmes. The grains were not found in rod, tubing, or built-up optical silica, or in general in silica which had been repeatedly reheated and worked.

Having a much larger dilatation than the glass, the quartz grains would be expected to produce radial tension and circumferential compression in the surrounding material. Rayleigh showed that this was in fact the character of the stress, by comparison of the birefringence with that produced by driving a conical plug into a sheet of celluloid, which produces just the opposite strain to that in the glass.

Why these grains of quartz should persist with such sharp outlines is not clear. Possibly they were protected by being caught up in a minute gas bubble during the principal period of fusion.

Indirect evidence on melting-points

Thermodynamic calculation of melting-points

Wietzel [29] has constructed tentative "*A-U* diagrams" (curves of the change of total energy and the change of maximal work or Helmholtz free energy, with temperature) for the reactions quartz ⇄ glass and cristobalite

[27] Brun, A., *Variations de l'indice de refraction du quartz provoquées par la calcination,* Arch. sci. phys. nat. (1896), (4), **2**: 657-658.
[28] Rayleigh [IV], Proc. Roy. Soc. (1921), **98**: 284-296.
[29] Wietzel, R., article cited in V, note [13].

⇄glass. The temperatures at which $A = 0$, that is, the melting temperatures, turned out to be: for quartz, 2300°C; for cristobalite, 4000°C. These are absurdly high, indicating that the heat capacity of vitreous silica obtained by extrapolating down from 19°K to absolute zero is very considerably in error. Until more exact heat-capacity data are available between 4° and 19°K, it will not be possible to calculate the melting-points from thermodynamic data. (See, further, Chapter XIX.)

Extrapolation of liquidus

An indirect indication as to the melting-point of a crystalline solid may be had by extrapolating its liquidus curve in the temperature-concentration diagram of a two-component or three-component system in which the substance in question is one of the components, and from which it crystallizes in the pure state.

In a two-component silicate system from which silica separates as cristobalite the curve may be expected to terminate in the melting-point of pure cristobalite, hence its direction furnishes some indication of where that melting-point is likely to be found.

Reasoning in this way from data on the system $SiO_2 : MgO : CaO$, Bowen [30] came to the conclusion that the melting-point of cristobalite must be considerably higher than 1625°, and probably higher than 1685°. This was confirmed by Ferguson & Merwin, as we have seen. The range of possible extrapolation has later proved to be limited, however, by the fact that two liquid phases occur in this and similar silicate systems, and the curve which rises on the silica side of the most siliceous eutectic is interrupted.

Possibility of a variable metastable melting-point for cristobalite

As will be shown in the discussion of the high-low inversion of cristobalite, this modification of silica probably varies in its internal constitution according to the temperature at which it was formed, and perhaps also according to other conditions, such as the modification out of which it was formed. These differences of constitution show themselves in a variable high-low-inversion point. They might naturally be expected to affect also the melting-point, in case the specimen of cristobalite were heated so rapidly that it did not have time to attain the internal equilibrium corresponding to its temperature. One "variety" of cristobalite might differ from another in melting-point, and both temperatures might differ from the true melting-point of cristobalite heated slowly enough to be in equilibrium; just as quartz and tridymite have melting-points of their own though both are unstable at their melting temperatures.

[30] Bowen, N. L., Amer. J. Sci. (1914) 38: p. 218.

If such an effect exists, it has not been proved experimentally. Although the possibility still remains that some of the quoted differences in melting-point obtained by different observers may be thus explained, the evidence is, so far, negative.

Ferguson & Merwin [31] noted that specimens of cristobalite formed at 1350° and at 1550° showed no observable difference in their melting phenomena. Rieke & Endell [32] found no differences in the behavior of three kinds of cristobalite at 1650-1700°, namely, (1) cristobalite from silica glass; (2) cristobalite from Norwegian pegmatite quartz; (3) cristobalite from Brazilian chalcedony.

Possible effect of fine subdivision

The effect of fine subdivision on the melting temperature of cristobalite may possibly be great enough to account for some of the minor discrepancies in the melting-point data, such as the difference between Ferguson & Merwin's 1710° and Rieke & Endell's 1685. Against this must be cited the fact that Rieke & Endell got the same melting-point on a cristobalite of normal density, made from vitreous silica, as on two cristobalites of subnormal density, made from pegmatite quartz and from chalcedony,—subnormal, presumably, partly because of their very fine state of subdivision and their submicroscopic and inaccessible pores. I do not believe it likely that fine subdivision of cristobalite will account for differences in its melting-point of more than 10°.

Historical notes on the fusion of silica

Temperatures of 1700°C or more were not readily accessible, at least for experimental purposes, to investigators in the 18th century and earlier. It was the invention of the oxy-gas and oxy-hydrogen burners that started the era of high-temperature research.

The earliest record of the fusion of quartz is that by Marcet [33] (1813) who melted small needles of quartz in an alcohol flame fed with a horizontal jet of oxygen. Clarke [34] (1821) noted that white opaque quartz could be melted in his oxy-hydrogen blowpipe to form a substance as limpid and transparent as rock crystal, but remarked that "the gaseous fluid which escapes during the fusion of pure silica, has never been collected, and, of course, remains unknown."

Gaudin,[35] in 1839, drew threads and made drops of transparent fused silica and exhibited them to the Academy at Paris. He also noted that the sand-

[31] Ferguson & Merwin, article cited in V, note [2].
[32] Article cited in V, note [16].
[33] Marcet, A., *On an easy method of procuring a very intense heat,* Annals Philos. (1813) **2**: 99-100.
[34] Clarke, Edward D., *Observations upon the gas blowpipe,* etc., Annals Philos. (1821) (2), **1**: 419-426.
[35] Gaudin, *Sur les propriétés du cristal de roche fondu,* Compt. rend. Acad. Paris (1839) **8**: 678-679, 711-713.

tone near Paris, instead of fusing to a transparent glass, yielded silky threads nd pearly drops. He seems to have been the first investigator who succeeded n working the glass.

In 1856 Deville[36] described his "forge à haute température," usually known s "Deville's coke furnace." In this he melted 30 grams of quartz sand to a lass resembling Gaudin's, but noted that the glass had not reached a tempera- ure of true liquidity. The sand was melted in a graphite crucible and, to judge rom the conditions described, was heated above the melting-point of platinum, 755°.

Investigators of more recent date have succeeded in making at least ap- roximate quantitative measurements of the temperature, and their results ave already been considered in this chapter.

The crystallization of vitreous silica

Fused silica is thermodynamically unstable at all temperatures below 710°, the melting-point of cristobalite. But, like the silicate glasses in eneral, its molecular sluggishness at atmospheric temperatures is so great hat no movement of the molecules toward symmetrical crystalline arrange- nent has been detected. Only on heating to red temperatures or higher oes the silica gain sufficient mobility to begin crystallizing.

This crystallization is commonly called "devitrification," as it usually esults in converting the transparent homogeneous glass into a white halky mass of minute crystals.

If the glass were to devitrify directly to the most stable crystalline nodification, it would form quartz below 870°, tridymite between 870° nd 1470°, and cristobalite between 1470° and the melting-point, 1710°. Usually, however, the product of devitrification is cristobalite alone.

Permutation (10). Vitreous to cristobalite

Between 1470 and 1710° cristobalite is the stable phase, to which the lass may be expected to change, and does change, when given an oppor- unity. But even *below 1470°*, at temperatures where tridymite is the table phase, the glass still crystallizes first to cristobalite when heated n the absence of a flux or solvent. No marked difference has been noted n the phenomena above and below 1470°.

Phenomena

The most striking fact about the crystalliation of vitreous silica to ristobalite is that it begins only at the surface and proceeds inward.

This crystallization from the surface furnishes the principal reason

[36] Deville, H. Sainte-Claire, *Mémoire sur la production des températures très-levées*, Ann. Chim. et Phys. (1856), (3), **46**: 182-203.

why opaque, translucent, or impure varieties of vitreous silica devitrify so much more rapidly than the pure homogeneous glass. The opaque and translucent varieties, such as "vitreosil," contain many fine pores and bubbles, furnishing a large total surface at which crystallization may begin. Glass made from impure materials may contain many small undissolved grains of impurities in addition to the bubbles and pores, still further increasing the devitrifying surface.

The decided contrast between the homogeneous and the inhomogeneous varieties is shown by the following comparative test[37] made by putting tubes of about 5 mm outside diameter and 0.5 to 1 mm wall through the regular burn in a porcelain kiln (maximum 1450°C):

Material	Final Density	Percentage of Cristobalite
Vitreous Silica from quartz crystal (Heraeus).....	2.21	0
"Vitreosil" (Deutsch-englisches Quarzschmelze, Pankow).	2.26	40
"Sidio III" (Dr. Voelker & Co., Beuel am Rhein).....	2.25	35

Another effect of impurities may be to produce at the point of contact a small amount of lower-melting and more fluid silicate which acts as a "flux" to encourage the crystallization. This fluxing effect was observed by Rieke & Endell[38] in homogeneous fragments heated to 1450° in a porcelain kiln; although the devitrification was very superficial, it was noticeably influenced by the traces of alkali left on the glass in handling.

Speed of crystallization

The rate of crystallization of pure homogeneous vitreous silica into cristobalite is greatly influenced by the following two factors: (1) the degree of subdivision, (2) the temperature.

Powdering the glass greatly increases the rate at which it crystallizes at a given temperature. This effect has not been quantitatively studied, but it apparently is only the direct corollary of the fact that the crystallization proceeds only from the exposed surface of a fragment. The greater the total surface of a given weight of glass, therefore, the faster it devitrifies.

The effect of temperature is better known. As in most chemical reactions, the rate increases very rapidly with the temperature.

At 1000° the rate of crystallization of pure homogeneous vitreous silica is inappreciable under most laboratory conditions. After heating powdered vitreous silica in a closed unglazed porcelain crucible for 35 days at a temperature just below the melting-point of gold (1063°) Joly[39] found that radial spherulites had formed in the glass.

[37] Rieke, R., & Endell, K., *Ueber die Entglasung von Quarzgläsern*, Silikat Zeitschr. (1913) 1: 6-12.
[38] Article cited.
[39] Article cited in note [49].

The crystallization becomes readily observable about 1200°, and rapidly increases at higher temperatures. The devitrification of the powdered glass

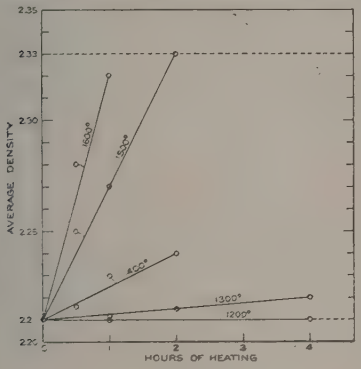


FIG. VI.2.

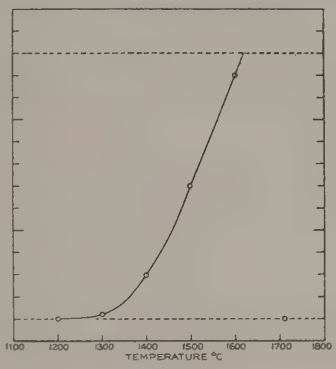


FIG. VI.3.

FIG. VI.2.—Experimental data on the rate of formation of cristobalite by devitrification of vitreous silica, as indicated by the average density. (Endell & Rieke, 1912.)

FIG. VI.3.—Part of the data of Figure VI.2 replotted to show the effect of temperature on the amount of vitreous silica devitrified in one hour.

is practically complete within 6 days at 1160°, 3 days at 1200° (Day & Shepherd),[40] 2 hours at 1500°, and 1 hour at 1600°.

TABLE VI.1.

EFFECT OF TEMPERATURE AND TIME ON THE CRYSTALLIZATION OF POWDERED HOMOGENEOUS VITREOUS SILICA.

Time of heating	1200°C		1300°C		1400°C		1500°C		1600°C	
	Sp. gr.	Per cent crist.	Sp. gr.	Per cent crist.	Sp. gr.	Per cent crist.	Sp. gr.	Per cent crist.	Sp. gr.	Per cent crist.
.....	...	...	...	...	2.216	5	2.25	34	2.28	60
.....	2.21	0	2.212	2	2.23	17	2.27	50	2.32	90
.....	...	...	2.215	5	2.24	25	2.33	100	...	...
.....	2.21	0	2.22	10	...	...	...	...	...	...

At temperatures from 1300 to 1600°C the amount of cristobalite formed from finely powdered pure homogeneous vitreous silica is approximately proportional to the time of heating, according to the measurements of Rieke & Endell,[41, 42] shown in Table VI.1, and plotted in Figures VI.2 and VI.3. They

[40] Article cited in IV, note [4].

[41] RIEKE & ENDELL, article cited in note [27].

[42] ENDELL & RIEKE, *Über die Bildung des Cristobalits aus Quarzglas und über eine reversible Zustandsänderung bei 230°*, Tschermak's Min. Petr. Mitt. (1912) 31: 501-512.

estimated the proportion of cristobalite by powdering the sample and determining its average density with a pyknometer. The density rises from 2.21 for the original vitreous silica to 2.33 for pure cristobalite.

The data obtained in this way are not highly exact, and it is very unlikely that the true curve of change at a given temperature can be a straight line throughout its course. The evidence is sufficient to show, however, that the change is not logarithmic, as it is for the transformation of quartz to cristobalite (Fig. V.1).

Endell & Rieke [43] also observed that vitreous silica (from Heraeus) was completely crystallized to cristobalite by one heating in a porcelain kiln (18 hours above 1200°, maximum 1450°).

They state that the rate "reaches a maximum at about 1600° and then falls off rapidly up to the melting-point". There is nothing in the data to indicate the existence of any such maximum. It seems to be purely an inference, drawn from analogy with the crystallization of undercooled solutions, molten salts, and organic compounds. There may be such a maximum for vitreous silica, but there is no evidence to show at what temperature it occurs.

Effect of gases

The rate of crystallization of vitreous silica to cristobalite may also be influenced by the composition of the gas with which it is in contact. It seems fairly certain that water vapor accelerates the devitrification. As to the effect of other gases, the evidence is not sufficient, and comparative experiments are needed.

Hahn [44] noted in 1903 the strong accelerating influence of water vapor on the crystallization of vitreous silica. In studying mixtures of CO and H_2O in a bulb of the glass he found that it crystallized rapidly above 1100°, becoming leaky before measurements could be made on the gases.

Seger & Cramer,[45] comparing "vitreosil" with titanium- and zirconium-bearing glasses, found that 1 hour at 1550°C in a granular-carbon electrical-resistance furnace caused a slight superficial devitrification of tubes of vitreosil, which was intensified by 3 hours' heating at the same temperature, though not sufficiently intensified so that a crystalline layer could be peeled away. This indicates a slower rate of devitrification than is usually found at so high a temperature, but the difference is not so marked that we can deduce a restraining effect of carbon monoxide or, conversely, an accelerating effect of oxygen.

Thomas [46] thought that he had found an accelerating effect of carbon monoxide, but his results are rather uncertain and Michie [47] thinks that alkaline vapors from his unprotected carbon furnace tube had an unknown but variable influence.

[43] Article cited in V, note [15].

[44] Hahn, Ber. Int. Kongr. Angew. Chem. (1903) 1: 714.

[45] Seger, H., & Cramer, E., *Quarzgläser,* Keram. Rundschau (1913) 21: 177-178

[46] Thomas, Felix, *Siloxyd, ein höherwertiger Ersatz des Quarzglases,* Chem.-Ztg. (1912) 36: 25-27.

[47] Michie, A. C., *Zur Frage der Entglasung von Quarzglas,* Chem.-Ztg. (1913) 37: 589-590.

Effect of previous thermal history

Another factor in the crystallization of vitreous silica, and one on which there is no clear evidence, is its previous thermal history, particularly the amount of superheating. The temperature and the time of superheating are known to influence the starting of crystallization, and perhaps its rate, in molten metals and organic compounds, so the same effect is to be expected in silica. Perhaps part of the reason why clear transparent vitreous silica devitrifies less readily than the silky or opaque glass is to be found in a greater degree of superheating of the liquid silica above 1710° in making the clear glass. This remains to be shown, however, since the effect of free surfaces in starting crystallization is qualitatively sufficient to explain the difference.

In making some experiments on the thermal dilatation of liquid silver Mr. Hostetter and I found that after one of the runs the vitreous silica disks which we used as our known displacement-volume had partially crystallized. The maximum temperature was 1445° and the glass had been above 1100° about 1½ hours. These disks had been cut from a block of glass made by Day & Shepherd [48] which contained a number of brown spots and streaks of elemental silicon. We found that the crystallization of the disks had begun in the clear parts of the glass and that the brown streaks were less devitrified or not devitrified at all. The presence of silicon indicates that the portion containing it has been in contact with the graphite container and has been heated hotter than the rest of the glass. This evidence supports the view that the more highly heated the glass, the less readily it crystallizes.

Miscellaneous observations on devitrification

Joly [49] seems to have been the first to note definitely the crystallization of vitreous silica. He observed incipient crystallization in the form of radial spherulites, in fragments of powdered vitreous silica after 35 days' heating at a temperature just below the melting-point of gold (1063°C). The powdered glass was contained in a covered unglazed porcelain crucible over a Bunsen burner.

In the course of his experiments on making fused quartz Herschkowitsch [50] found that some of his pieces came out of the furnace in the form of a white, porcelain-like material, which proved under the microscope to be a mixture of amorphous and crystalline grains. Tests soon showed that the porcelain-like material could be made by heating fragments of the glass over a blast flame for several hours. He supposed that the product of crystallization is quartz, whereas it is now known to be cristobalite.

Heraeus [51] in 1903 observed devitrification of the outer surface of a vitreous silica tube which had been heated for 3 hours at 1300°, and observed the sudden

[48] Day, A. L., & Shepherd, E. S., *Quartz glass,* Science (1906) **23**: 670-672.
[49] Joly, J., *Vitrified quartz,* Nature (1901) **64**: 102.
[50] Article cited in V, note [39].
[51] Article cited in note [23].

appearance of this devitrification when the tube had cooled nearly to atmospheric temperature after the first heating, a phenomenon now understood to be due to the inversion of the cristobalite at 200-270°. Heraeus thought that the effect was due to dust, and was confirmed in this belief when he found no devitrification after a similar heating in a closed platinum tube. Subsequent experiments by others, such as the experiments already cited, show that the presence of dust is not necessary to start devitrification at 1300°.

The true explanation of the difference observed by Heraeus is not known; perhaps the second tube had been made at a higher temperature and was a more homogeneous piece of glass than the first.

Incidentally to a series of strength tests, Blackie [52] made microscopic observations of the changes in appearance of opaque and transparent vitreous silica heated at 1124-1353°. Crystallization occurred on the outer surfaces and also on the surfaces of bubbles, especially bubbles open to the air or near the surface, after 4 to 8 hours at 1122-1188°. After 4 hours at 1275° a few specimens of the "opaque" glass showed crystals within the mass of glass as well as a "micro-crystalline structure" in some areas; and similar effects were noted in almost all the "opaque" specimens which were heated 4 hours at 1353°. Transparent specimens, however, crystallized only at surfaces (external or bubbles). The crystals are called "tridymite" but were probably cristobalite. The effect of access to air in promoting crystallization was especially noted.

Koenigsberger [53] (1912) states that vitreous silica capillary tubes of 20 mm outside and 0.5 mm inside diameter, in which mercury was being heated to determine its critical temperature, "showed rapid devitrification (the well-known inversion to cristobalite) and burst, when half filled with mercury, at about 1000°C." This was evidently only a rough estimate of the temperature, because the experiments had to be made within a period of a few seconds on account of the swelling and bursting of the tubes. The temperature of devitrification was in fact above 1000°, and clear vitreous silica tubes used in subsequent similar experiments stood up to about 1350° without devitrifying.[54]

Crookes [55] found that a vitreous silica bulb devitrified sufficiently in 31 hours at 1300° so that there was an easily measurable leakage of air through the wall when the bulb was evacuated. The leakage continued both at 1300° and at atmospheric temperature. A micro-photograph showed a minutely cracked or crazed surface on the translucent white glass.

Crookes [55] has reported that the evaporation of 100 mg of pure radium bromide at 100° in a clear transparent vitreous silica dish produced dull, roughened patches on its surface, resembling under the microscope the cracked surface of silica devitrified by heating at 1300°. It has not been proved that this is a real devitrification. If it is, we have here a very interesting cause of crystallization which deserves further study.

No such effect was observed by Crookes on the surface of glass bottles

[52] Blackie, A., *On the behaviour of fused silica at high temperatures*, Trans. Faraday Soc. (1911) **7**: 158-165; Coll. Res. Nat. Phys. Lab. (1911) **8**: 139-151; Chem. News (1911) **104**: 77-79, 86-88.

[53] Koenigsberger, J., Chem.-Ztg. (1912) **36**: 1321.

[54] Koenigsberger, J., Correspondence with the author (1923).

[55] Crookes, W., *On the devitrification of silica glass*, Proc. Roy. Soc. London (1912) A, **86**: 406-408.

of silica bottles in which radium salts had been kept at atmospheric temratures for several years.

Brun [56] reported having made a new kind of cristobalite by first fusing ica (modification not stated) in an oxy-hydrogen flame and then heating for 5 hours at 1600°. He stated that the cristobalite so produced differed om natural cristobalite and called his preparation "cristobalite Σ." There is thing in the properties he gives, however, to prove that it differs in any sential respect from any other cristobalite.

"Incipient" crystallization

Certain small changes have from time to time been observed in the operties of vitreous silica as a result of heating it to high temperatures. t the same time no actual crystals have become visible. For instance:

Boys [57] observed that vitreous silica fibers are "spoiled" by being reheated. rrelfall [58] and Shenstone [59] also refer to this fact. Shenstone suggested that st particles on the fibers might be responsible.

Houldsworth & Cobb [60] made several experiments on the effects of high mperatures on the dilatation-coefficient and refractive indices of vitreous ica. They used the commercial variety of the glass known as "vitreosil." Their measurements of dilatation, made on various substances, were all fferential, the standard reference substance being vitreosil in the form of tube. To obtain a check on its constancy, a second piece of vitreosil was sted in the apparatus at the beginning of the experiments, and again after months, after the tube of the apparatus had been heated many times to 00°, which was the limit of their expansion tests. The test piece showed actly the same expansion curve as at the beginning, namely, zero expansion om 15 to 800° and a barely detectable contraction from 800 to 1000°. This parent contraction probably represents a difference in temperature between e outer parts of the expanding apparatus, and not a difference between the o specimens of vitreosil. Whatever its cause, the exact repetition of the rve of the test piece of vitreosil shows that the many heatings to 1000° dergone by the standard silica reference tube of the apparatus caused no ange in its expansion and presumably no change in its constitution.

Other pieces of vitreosil served for the tests shown on p. 104.

The authors interpret these results as indicating the conversion of part the vitreosil into tridymite. It seems more likely, in view of the other ta already considered, that their material of index 1.468 to 1.481 was really very fine-grained mixture of cristobalite and glass. The expansion curve dicates that the amount of cristobalite was small.

[56] Brun, A., *Cristobalite (simili) ou cristobalite sigma* (Σ), Soc. Helvet. Sci. Nat. 912).
[57] Boys, C. V., Proc. Phys. Soc. London (1887) **9**: 8-19.
[58] Threlfall, R., *Laboratory arts.*
[59] Shenstone, W. A., *Vitrified quartz,* Nature (1901) **64**: 126.
[60] Article cited in V, note [23].

Temperature °C	Time of heating. Hours	Expansion to 1000° after heating	Index of refraction o powdered material
1150-1170	4	Same as original	Less than 1.468
1410-1430	3	Same as original	Mostly less than 1.4 Small portion betwe 1.468 and 1.481
1510-1555	2½	No change to 200° 0.05 per cent expansion 200 to 1000°	⅓ to ½ between 1.4 and 1.481. Rest le than 1.468

Although hot vitreous silica can usually be quenched in water witho damage, Rayleigh [61] found that a polished optical disk which had been heate to about 1000° for 2 hours and was then quenched in water, showed a superfici network of fine cracks.

Considerable changes in rigidity have been observed as a result of heatin fibers to a few hundred degrees; the data will be discussed in Chapter XXI

These changes may possibly be attributed to the beginning of rearrange ments within the material, rearrangements leading ultimately to its crystalliz tion into cristobalite, but a minute study of the changes as related to time an temperature will be necessary before their character can be understood.

Permutation (11). Vitreous silica to tridymite

The direct crystallization of vitreous silica to tridymite in the pure dr state has not been observed at any temperature.

At temperatures *below 870°* tridymite can be obtained directly fro vitreous silica by heating the powdered glass with sodium tungstate 800-870°. Being an unstable phase, this tridymite then inverts furth into quartz.

Between 870 and 1470° vitreous silica when heated in the dry sta first goes through the cristobalite stage before changing into tridymit the stable form. Even when heated with a flux (sodium tungstate or mixed alkali silicate) in this temperature range, not all the glass go direct to tridymite, but some cristobalite is formed at the same tim (Fenner).

Above 1470° the formation of tridymite from vitreous silica, thoug logically possible as an intermediate stage, has never been observed.

Speed of crystallization

The rate of inversion of vitreous silica to tridymite is very slow. A 865°, in the presence of sodium tungstate, the powdered glass is complete converted into tridymite within 11 hours, some of this tridymite havi

[61] Rayleigh, Proc. Roy. Soc. London (1921) **98**: p. 294.

meanwhile recrystallized further into quartz, the stable modification at this temperature (Fenner).

The experimental data

Brun[62] observed that the action of mixed vapors of KCl and NaCl on powdered vitreous silica at temperatures between 800 and 1000° yielded hexagonal crystals of tridymite within 11 hours.

Day & Shepherd[63] observed that tridymite was formed from the glass at 800° and higher, when it was heated with sodium tungstate, vanadic acid, or potassium chloride mixed with one-fourth its weight of lithium chloride.

An important fact which these investigators did not observe was that below 870° the tridymite formed from glass is not the final stable product. It is so only above 870°.

Day, Shepherd & Wright[64] reported the formation of "tridymite" direct from vitreous silica at 1000° and above. The product was subsequently found to be cristobalite (see p. 62).

Hahn[65] states that a vitreous silica bulb containing gaseous H_2O and CO devitrified rapidly above 1100° with the formation of tridymite whose presence was shown microscopically in a thin-section. (See p. 100.)

Permutation (12). Vitreous silica to quartz

It is doubtful whether quartz has ever been crystallized directly from vitreous silica. At temperatures *below 870°*, where quartz is the stable phase, there is no observable evidence of crystallization produced by heat alone, while fluxes or "mineralizers" produce first one of the unstable modifications which then changes further into quartz.

Above 870° quartz has never been produced from vitreous silica, either directly or indirectly.

The experimental data

Brun[66] reports having formed quartz direct from vitreous silica with the aid of mixed vapors of KCl and NaCl at 700-750°. The initial effect observed by Brun was the production of very fine fibers, parallel or grouped in spherulites; these were probably cristobalite or tridymite, not quartz, as stated by Brun. The properties of this material were not determined. Continued heating, totaling 40 hours, then produced recognizable crystals of quartz. After 3 to 4 days, optically homogeneous crystals of quartz 3 mm long were obtained.

Fenner found that in the presence of sodium tungstate, at 800-850°, the glass is first converted into the unstable form tridymite, which then changes further into quartz.

Day & Shepherd had already noted that tridymite was formed from the

[62] Brun, A., *Cristallisation du quartz,* Arch. sci. phys. nat. (1908) **25**: 610-611.
[63] Article cited in IV, note [4].
[64] Article cited in V, note [8].
[65] Hahn, Discussion cited in note [44].
[66] Brun, A., article just cited.

glass at temperatures of 800° and higher in the presence of three different solvents, namely, sodium tungstate, vanadic acid, and potassium chloride mixed with one-fourth its weight of lithium chloride. They did not observe the further change of this tridymite into quartz and so concluded erroneously that 800° was the equilibrium temperature of quartz and tridymite. (See p. 50.) Below 760° they obtained only quartz.

When heated at 300° in the presence of water and ammonium fluoride for eight hours, the glass is converted into a fibrous product which "corresponds with quartz in its optical properties." [87]

Historical note on the devitrification of vitreous silica

Although the fusion of quartz to a glass had been accomplished several times before 1839, the devitrification of this glass had not been observed until Gaudin, in that year, tried the experiment of heating one of his rods of glass in a platinum tube to a reddish-white temperature and letting it cool slowly. The rod was found to have been completely disintegrated by this treatment. Gaudin offered no explanation, but evidently had in mind as a possible analogy the splintering of ordinary soft glass when heated and then chilled in water, for he notes the fact that vitreous silica so treated remains undamaged.

The true explanation seems to have been first perceived by Joly in 1901 (see p. 101).

The vaporization of silica

One phase of silica remains to be considered, namely, the gas or vapor phase. Since gases are miscible in all proportions, there can be only one such phase, whose density depends upon the temperature and pressure.

The relations of gaseous silica to the liquid and crystalline forms are in every way analogous to the relations of gaseous water, or, as we usually call it, "water vapor," to liquid water, ice, and the other crystalline forms of H_2O. The great difference is that the equilibrium pressures of water are easily measurable at atmospheric temperatures, while the pressure of gaseous SiO_2 in equilibrium with its crystalline or liquid forms becomes appreciable only at temperatures near 1700°C.

We must logically expect that at any given temperature there is a certain *vapor pressure* of silica at which the gas is in equilibrium with the other phase or phases present. A higher external pressure causes the gas to condense, while a lower pressure leads to further vaporization. We have paid little attention to the gas phase thus far, because its pressure is so extremely low at most accessible temperatures that it is negligible.

The addition of a gas phase to the 4 phases previously described (3 crystalline and 1 liquid) adds 8 more to the 12 permutations which have already been considered. For logical completeness the new ones are listed below, although there will be little to say about most of them.

[87] Endell & Rieke, article cited in V, note [25].

(13) Quartz to vapor
(14) Tridymite to vapor
(15) Cristobalite to vapor
(16) Liquid (glass) to vapor
(17) Vapor to quartz
(18) Vapor to tridymite
(19) Vapor to cristobalite
(20) Vapor to liquid (glass)

False vaporization

Although there is no question that silica is appreciably volatile at a white heat, not all of the observed vaporization of silica is a true evaporation of the compound SiO_2.

In addition to its true evaporation there is under certain conditions an apparent evaporation which is not due to vaporization at all but to reduction and reoxidation. In a reducing atmosphere, such as exists in a carbon-tube electric furnace, abundant white vapors of silica are frequently seen, which result from (1) the reduction of SiO_2 to Si, (2) volatilization of the silicon, which is much more volatile than silica, and (3) re-oxidation of the Si to SiO_2 either through admixture with air or through recombination with the original oxygen in a cooler part of the furnace. The reactions may be pictured as follows:

Hot part of furnace	Cold part of furnace
$SiO_2 + 2C = Si + 2CO$	$Si + 2CO = SiO_2 + 2C$
$SiO_2 + 2CO = Si + 2CO_2$	$Si + 2CO_2 = SiO_2 + 2CO$
$SiO_2 + 2H_2 = Si + 2H_2O$	$Si + 2H_2O = SiO_2 + 2H_2$
	$Si + O_2 = SiO_2$

The equilibrium of these reactions has been studied by Wartenberg[68] (1912) and the transference of silica by reduction and reoxidation has been shown by him experimentally at a temperature as low as 1350°.

Dufour[69] has also demonstrated it by heating three vitreous silica tubes to the same temperature and passing through them hydrogen, oxygen, and carbon monoxide, respectively, all at the same rate. A deposit of sublimed silica was formed in the hydrogen tube, but none in the other two. There was also an absence of sublimation in nitrogen under similar conditions. Wartenberg has since shown that the reducing activity of carbon monoxide on silica is much less than that of hydrogen, which is probably the explanation why no sublimate was observed in the carbon monoxide tube. Three different blast flames were also tried by Dufour on the same fragment of silica: one of carbon monoxide and oxygen, one of illuminating gas and oxygen, and one of hydrogen and

[68] Wartenberg, H. v., *Über die Reduktion der Kieselsäure,* Zeitschr. anorg. Chem. (1912) **79**: 71-87.

[69] Dufour, A., *Réduction de la silice par l'hydrogène,* Compt. rend. Acad. Paris (1904) **138**: 1101-1103.

oxygen. The silica lost 0.5 mg in the first, 24 mg in the second, and 40 mg in the third, when heated to the same temperature for the same time.

Volatilization as element or hydride in an atmosphere of hydrogen is also shown by the common experience of the embrittlement of platinum in the join presence of silica and hydrogen. For example, Shepherd [70] showed by analysi of the brittle platinum that its gain in weight was equal to the amount of silico found in the metal. Furthermore, the embrittlement takes place even whe the platinum and silica are not in contact.

All data on the volatility of silica in carbon arc furnaces, in carbon-tube electrical resistance furnaces, and under conditions in general where carbon monoxide, hydrogen, or other reducing gases may be present, are subject to the uncertainty that it is impossible to tell how much of the volatility was due to reduction and how much to true evaporation.

Among such observations may be cited:

Cramer [71] (1892). Quartz heated to above the melting-point of platinum in a carbon crucible in a Deville coke furnace lost about 40 per cent of its weight in 2 hours.

Moissan [72] (1893). Quartz volatilized rapidly from a carbon crucible in a carbon arc.

Schützenberger [73] (1893). Silica lost weight when heated in a carbon crucible to a white heat in an air-blast furnace.

Moissan [74] (1904). When lime (CaO) was heated in a graphite boat within a vitreous silica tube containing hydrogen, enough SiO_2 sublimed, at temperatures above 1200°, to form needles of a silicate over the surface of the lime.

Day & Shepherd [75] (1906). Quartz volatilized freely about 2000° when fused electrically in a graphite crucible.

Stein [76] (1907). Quartz volatilized above 1750° when melted in a carbon crucible in a carbon-tube resistance furnace, at the rate of 3.5 g in ½ hour, original weight having been 5 g.

An unknown author [77] ("Ri") has published analyses of 3 clays, a feldspar a kaolin, and kaolin mixed with magnesia, lime, or potash, before and afte heating in a carbon crucible in an arc furnace at 100 volts and 100-150 amperes In every case there is a diminution in the percentage of SiO_2, amounting to 0.5 to 7.9 per cent. This means that SiO_2 has been lost more rapidly than one or more of the other oxides present. The amount of true volatilization as compared with volatilization through reduction by carbon is unknown.

[70] Shepherd, E. S., Rankin, G. A., & Wright, F. E., Amer. J. Sci. (1909) **28** 293-333, p. 300. Also Shepherd, E. S., Journ. Geol. (1925) **33**: p. 305.
[71] Cramer, E., *Über die Flüchtigkeit der Kieselsäure,* Zeitschr. angew. Chem **1892**: 484-486.
[72] Moissan, H., *Sur la volatilisation de la silice,* etc., Compt. rend. Acad. Pari (1893) **116**: 1222-1225.
[73] Schützenberger, P., Compt. rend. (1893) **116**: 1230.
[74] Moissan, H., Compt. rend. (1904) **138**: 243-245.
[75] Day & Shepherd, article cited in note [70].
[76] Stein, article cited in note [15].
[77] Deutsch. Töpfer- u. Ziegler- Ztg. (1922).

ERMUTATIONS (13), (14), (15). QUARTZ, TRIDYMITE, OR CRISTOBALITE TO VAPOR

The direct volatilization of silica at temperatures below 1600° has not en proved.

Wartenberg measured the change of weight of a platinum boat containing ica (form not stated), at 1350°, in a current of air. The boat alone lost mg per hour, a familiar phenomenon, as platinum always loses weight the presence of oxygen. When filled with silica its loss of weight was 1.1 per hour. Within this limit of accuracy, namely, 0.2 mg per hour from ica contained in a small platinum boat, there is therefore no measurable latilization of silica at 1350°.

Cramer (1892) made an experiment at a somewhat higher temperature bout Seger cone 26, or 1600°) by heating a quartz crystal in a closed carbon ucible for about two hours, finding its weight constant (limit not definitely ted but presumably 1 mg in about 3 g) in spite of the reducing conditions.

PERMUTATION (16). LIQUID TO VAPOR

Only above the melting-point does the direct volatilization of silica come easily measurable. Qualitative observations indicate that the vapor essure then rises fairly rapidly, but the boiling-point, which is the tem- rature at which the vapor pressure equals 1 atmosphere, is not known.

The white opaque crust formed on vitreous silica while it is being worked the flame was ascribed by Shenstone to an effect produced by "the minute ces of alkaline metals present in most Brazil pebble, which are usually burnt in the processes" described by him. It is probable that the alkali, if present, s little to do with this phenomenon, for such deposits are always produced en the glass is heated in an oxy-gas flame.

The "ebullition" observed by Moissan was probably not true boiling, but escape of carbon monoxide formed by reaction between the molten silica the carbon crucible.

Ruff & Schmidt[78] concluded from measurements of the rate of loss of ight of SiO_2 in a graphite crucible lined with vanadium carbide that the ling-point is about 2200° at 1 atmosphere. Later experiments[78a] give a ling-point of not less than 2060° under 11 mm pressure, from which, by sonable assumptions, a boiling-point of 2600° at 1 atmosphere may be luced.

The condensation of silica vapor

The vapor of silica usually condenses into some very finely divided m, either crystalline or glassy. Since a special chapter is devoted to se and other "micro-forms" (Chapter X) only a few general statements the condensation of silica will be made here.

[78] RUFF, O., & SCHMIDT, P., Zeitschr. anorg. allg. Chem. (1921) **117**: 172-190.
[78a] RUFF, O., & KONSCHAK, M., Zeitschr. Elektrochem. (1926) **32**: 515-525.

Permutations (17), (18), (19). Vapor to quartz, tridymite, or cristobalite

Neither quartz nor tridymite has ever been shown conclusively to be product of the condensation of silica vapor in the absence of other su stances. Stein's statement that crystals of tridymite were formed fro the vapor in his carbon-tube furnace lacks confirmatory evidence and improbable.

The fine white powder which usually deposits is either the micr amorphous variety or is finely divided cristobalite.

Permutation (20). Vapor to liquid or glass

Sublimed silica has several times been found in vitreous form, usual as minute spheres.

Heraeus states that silica which had been vaporized in the oxy-hydrog flame during the fusion of quartz condensed to a white, fluffy powder, consis ing of distinct small spheres.

Moissan[79] (1893) found that the silica which volatilized from a carbon a furnace could be condensed to a bluish white powder, consisting chiefly small glassy spheres, easily visible with low magnification. Many of the had a depression or hollow at one point, which Moissan thought might indica a shrinkage on "solidification." The density was about 2.4, which is high f vitreous silica, but the rapid rate of dissolving in cold hydrofluoric ac indicates that the spheres were glass, and not a denser crystalline form. Th easily scratched ordinary glass. Moissan observed similar spheres on t inside of the glass globes of electric arc lights.

Stein observed that the silica which vaporized in his carbon-tube furna deposited partly as a thin film of glass over the inside of the tube. Below it the tube was a ring of aphanitic silica containing lime and above it a ring crystalline silica. The material of the film had a density of 2.28, which considerably too high for pure vitreous silica, and it seems not unlikely th it contained lime or some other basic addition which raised its density. T condensation of silica to form a continuous film of glass is therefore not prove

Historical notes

The volatility of silica seems not to have been recognized by the earli investigators who succeeded in fusing it, although they undoubtedly attain temperatures, under reducing conditions, at which the white smoke or chal deposit of volatilized silica should have been noticed.

Gaudin[80] (1839), who was the first to work vitreous silica, observed rapid volatilization in the flame, and proposed the hypothesis that its "perm nent viscosity" results principally from the "constancy of its temperature pr

[79] Moissan, article cited (1893).
[80] Article cited in note [35].

uced by continuous evaporation," evidently having in mind the constant temerature assumed by water and other liquids when boiling.

The first experiments on the subject were by Jeffreys,[81] in 1840. He noted ne corrosion of siliceous bricks by high-temperature steam and the deposition f siliceous crusts on stoneware placed in a cooler part of the furnace. This ıay have been a case of reduction and reoxidation. Next followed Cramer's xperiments in 1892, and the other experiments and observations which have een referred to in the preceding pages. No systematic and extended study f the true volatilization of silica has been made.

[81] JEFFREYS, JULIUS, *On the solubility of silica by steam,* etc., Proc. Roy. Soc. ond. (1840) **4**: 232-233.

Chapter VII. THE HIGH-LOW INVERSIONS

High-low polymorphism

The type of polymorphism now to be considered is decidedly different from the sluggish type described in the previous chapters. The most striking characteristics of the new type are its promptness and its ready reversibility. At a constant pressure, a change of temperature from lower to higher, or vice versa, is usually sufficient to bring about the inversion. I have therefore called this type "high-low polymorphism" in accord with the terms "high-quartz," "low-quartz," etc., adopted for the various modifications of silica (see p. 43). This kind of polymorphism is found in a great many substances, and deserves some general consideration here before we pass on to the details concerning the high-low modifications of silica.

The principal characteristics of this type are:

(1) The inversion occurs promptly when the inversion-temperature is reached, completing itself in some instances within a few seconds.
(2) The inversion is reversible, going in one direction when the temperature rises and in the opposite direction when the temperature falls.
(3) The difference in energy content between high and low modifications is relatively small.
(4) There is a "temperature hysteresis," the inversion starting at a slightly higher temperature on heating than on cooling.
(5) The inversion does not proceed from centers or nuclei but occurs simultaneously either throughout a whole crystal, or throughout a volume whose dimensions are large enough to be easily measurable. (See discussion in the paragraphs on experimental data.)

Types

Several kinds of high-low polymorphism, grading one into another may be distinguished experimentally. Benedicks [1] has called these "types I, IIa, IIb, III, and IV," and distinguishes among them according to the manner in which the physical properties change at and near the inversion point.

The distinction will be evident from Figure VII.1.

In type I the inversion occurs suddenly, without any abnormal variation in the course of change of the property which is being studied.

[1] Benedicks, C., *On allotropy in general and that of iron in particular,* J. Iron & Steel Inst. (1912) **86**: 242-274.

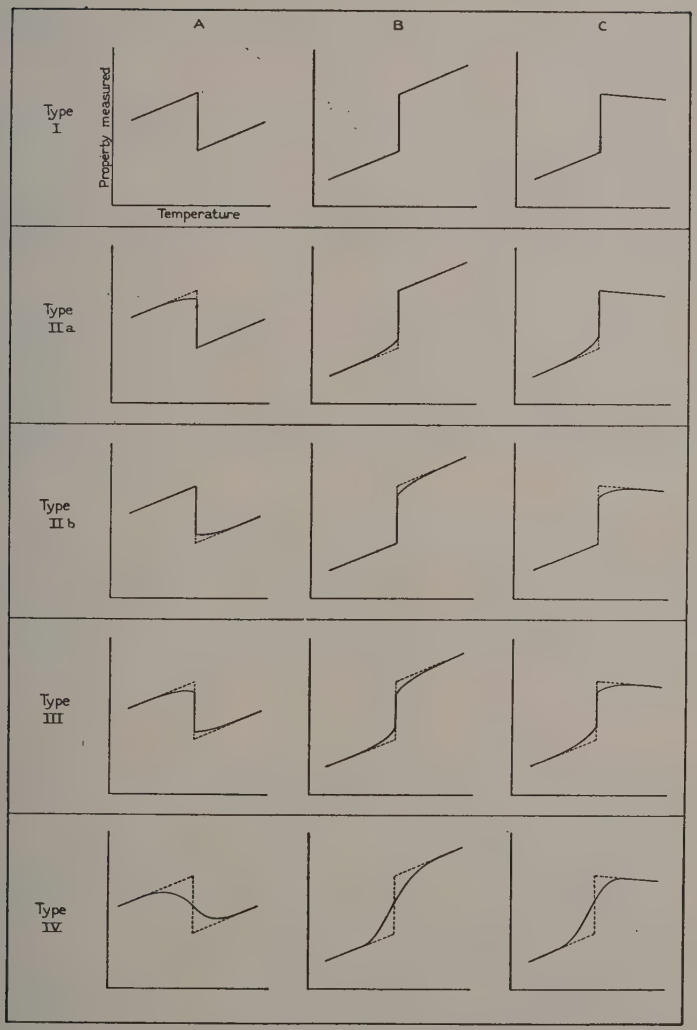


FIG. VII.1.—A classification of polymorphous inversions into types and varieties.

In types II and III there is a preliminary "warning" in the form of a gradually increasing departure of the property from the course followed at temperatures distant from the inversion. In type IIa this preliminary effect occurs below but not above the point; in IIb, vice versa; while in type III it occurs both above and below.

In type IV the sudden part of the change has decreased in relative amount until it has disappeared, and the curve of the property against temperature is continuous.

The five types may be further subdivided into varieties, according to the direction of change of a given property in each of the three parts of the curve. The total number of permutations of this kind is 8, of which 3 are shown in Figure VII.1, marked A, B, and C.

If experiment has shown that there is a definite change of symmetry associated with the inversion, then the curve of any directed property *for a single crystal* can not be of type IV. A continuous change of symmetry whether with respect to shape or with respect to any directed property is not conceivable. The curve *for an aggregate* of crystals may, however be of the shape of type IV, even though the inversion is really of type I II, or III, as will be seen in connection with the inversion of cristobalite (see p. 127).

The high-low inversions of silica

Silica offers one of the best examples of the contrast between the sluggish inversions, such as those between quartz, tridymite, and cristobalite, and the high-low (alpha-beta) inversions, such as are shown by each of these three principal forms. All of the high-low inversions of silica have the characteristics just described.

High-quartz and low-quartz

The inversion of low-quartz to high-quartz occurs with rising temperature at 573° ± 1°. The reverse inversion, with falling temperature, occurs about 1° lower.

The principal features of the high-low quartz inversion are:

(1) A gradual increase in the rate of change of all properties, beginning 50° or more before the inversion point is reached.
(2) An entire absence of such a preliminary effect on the high-temperature side of the inversion point;
(3) A change of symmetry at the inversion point;
(4) An abrupt change in nearly all of the physical properties at the inversion point.

The inversion is therefore of the type IIa (see Fig. VII.1).
Another noteworthy feature is

(5) The very small rate of change in properties above 573 as compared with the rate of change between 0° and 573°.

All of these features appear clearly in various figures later in this book, ustrating the dependence of the different properties of quartz upon the mperature. (See especially Figures XIX.1, XIX.6, XX.1, XX.4, XIII.8, XXXIV.3, XXXIV.7.)

Speed of inversion

The speed of the inversion is high. After the inversion has started may be completed throughout the crystal inside of a few seconds, if the ystal has a fairly uniform temperature. Wright [2] observed with a small ystal in the goniometer furnace that the inversion was completed in 2 5 seconds. Mügge [3] found that in a 0.03 mm plate the change was litzschnell" (quick as lightning).

General summary of the phenomena of the inversion

There is no evidence of the growth of a new phase from centers or iclei, as in the crystallization of a liquid. On the contrary, the crystal anges over as a whole from the one modification to the other. The incipal axis of symmetry remains unchanged in position, although the ial ratio changes.

There is decided mechanical instability in the crystal at the moment inversion. The volume and the elastic constants undergo very rapid anges (see XX and XXIII) and the crystal may bend or move, or en break into smaller pieces.

Sudden changes in optical properties also accompany the inversion. ne birefringence, and probably the other optical properties also, undergo ange a little in advance of the change of shape and volume, both with ing and with falling temperature.

After-effects

A commonly-observed effect of the inversion from high-quartz to low-artz is the production of twinning of the Dauphiné type. This will be scribed in greater detail in Chapter XII after the symmetry and twinning quartz have been discussed.

Aside from this twinning, a fragment,—or even a large crystal,—of re, homogeneous, unstrained quartz seems to be practically unaffected in operties at atmospheric temperature after the passage up and then down rough the high-low inversion at 573°, provided the heating has been iform and not too rapid. If the heating be so irregular or so rapid at there are considerable differences in temperature between large por-

[2] WRIGHT, F. E., *The change in the crystal angles of quartz with rise in tem-rature*, J. Washington Acad. Sci. (1913) 3: 485-494.
[3] MÜGGE, O., *Ueber die Zustandsänderung des Quarzes bei 570°*, Neues Jahrb. n. etc. (1907), Festband: 181-196, pl. 9.

tions of the crystal, one portion may invert in advance of another and the resulting stresses may break the crystal into smaller fragments. There is no residual effect in the substance itself. (See also p. 66.)

Constancy of the inversion temperature

Although I have given the inversion point as 573° ± 1°, it is not yet wholly certain that the point is as constant as this for all kinds of quartz.

The most accurate measurements of the high-low quartz inversion point are those by Bates & Phelps.[4] They found the rising-temperature inversion to be constant within 0.2°, occurring within the limits 573.2° and 573.4°. The falling-temperature inversion varied more widely, covering the range 572.7 to 572.0.° This was true for about ten specimens of quartz, obtained from different parts of the world.

Unfortunately for our present purpose the measurements were all made upon vein quartz in cut plates (2 × 10 × 30 mm) or large clear crystals, and it is not at all certain that the constancy found by Bates & Phelps would still hold good for quartz of different geologic origin.

According to Fenner,[5] the inversion occurs at 575° ± 2° with rising temperature and 570° ± 2° with falling temperature. These figures are in substantial agreement with the more accurate determinations of Bates & Phelps. Fenner found the point to be constant within 4° at the outside (573° to 577°) on rising and 5° (567° to 572°) on falling temperature for 14 different specimens of quartz, including 1 artificial and 13 natural specimens.

One specimen, however, was found which gave an inversion point with rising temperature of 564° to 569°, and with falling temperature, 556° to 560°, namely, about 8 to 10° lower than all the rest. This was a specimen obtained from basalt, found in association with zeolites. Treatment with HCl and heating at 1400° did not appreciably affect its inversion point. A possible explanation is the presence of some impurity in solid solution, but no solid solution in quartz has ever yet been proven, and this abnormal inversion point invites further study.

The possibility of a real variation of about 10° in the inversion point, depending upon the origin or history of the quartz, is by no means excluded, since a like variation of much greater magnitude is definitely proven for cristobalite.

As already mentioned, the inversion point with rising temperature was found by Bates & Phelps to be more constant than that with falling temperature. The variations in the latter have not been correlated with any other variable, so it is impossible to say whether they are due to different amounts of overheating (in temperature or time) after the inversion was passed on heating, or to some other factor.

[4] Bates, F., & Phelps, F. P., *The new fixed point on the thermometric scale*. Physical Rev. (1921) (2) **18**: 115-116.

[5] Fenner, C. N., article cited in IV, note [3].

The experimental data

The inversion temperature

Bates & Phelps' determinations, which I believe to be the most accurate ow available, were made by means of a platinum-platinrhodium thermocouple serted into a small hole drilled in the plate or crystal. The crystal was heated

Table VII.1.

Determinations of the High-Low Inversion Point of Quartz. Wright & Larsen, 1909.

Quartz plate	Rapid heating	Slow heating	Mean	Rapid cooling	Slow cooling	Mean	Mean of heating and cooling	Notes
I	576.8	576.7		574.9	575.2			
.28 mm	576.8	576.7		575.0	575.3			
thick	576.7	576.8		574.8	575.3			
	576.5	576.7		574.6	575.2			
	576.7	576.6		575.0	575.2			
	576.7			575.2				
	576.7			574.9				
	576.8			574.9				
	576.7			574.6				
				574.5				
	576.7	576.7	576.7					
				574.8	575.2	575.0	575.8	Original thermocouple
II	573.7	573.4		572.4	572.7			
232 mm	573.4	573.4		572.5	572.7			
thick,	573.4			572.5	572.6			
rea 20.4					572.6			
q. mm	573.4 †			572.4 †	572.8 †			
	573.6 †			572.6 †	572.8 †			
	573.5 †							
	573.4 †							
	573.5	573.4	573.4	572.5	572.7	572.6	573.0	New thermocouple
III	576.4	576.1 *		575.4	575.5			
224 mm	576.5	576.1 *		575.4	575.5			
thick,		576.2			575.7			
rea 6.8					575.6			
q. mm					575.4			
	576.5	576.1	576.3	575.4	575.5	575.5	575.9	New thermocouple
ean of I, II, and III....			575.5			574.4	574.9	

* Very slow heating. † Current in furnace reversed.

cooled at a very slow and uniform rate in an electric resistance furnace. time-temperature curve showed the temperature at which the thermocouple gan suddenly to depart from its regular curve of increase or decrease. With sing temperature, heat is absorbed at the inversion point, and the temperature lls behind that of the furnace, overtaking it again later. Conversely, with

falling temperature, heat is released by the inversion, and the temperature is thereby maintained for a time above its normal steady-cooling values. The heat effect of the inversion was observable even when the thermocouple was only placed close to a plate of dimensions 10×1.5 mm and not actually inserted into it.

Fenner's determinations, likewise, depended upon heating and cooling curves, but he used a differential thermel and made measurements on powdered samples instead of on large pieces.

Wright & Larsen[6] measured the inversion temperature on plates 0.22 to 0.28 mm thick, cut parallel to the axis, and resting on the junction of a platinum-platinrhodium thermocouple in a thermal microscope. The birefringence bands in a Babinet compensator were watched by one observer, and the exact temperature when the bands made their sudden shift was read on a potentiometer by a second observer. Two different thermocouples were employed: one which had been in use in the thermal microscope and another freshly drawn from wire which had been compared with the nitrogen thermometer by Day & Sosman.[7] The results are given in Table VII.1.

These results agree with those of Bates & Phelps in showing that the inversion with rising temperature is more constant than that with falling temperature.

The difference between plates II and III is not necessarily a real difference in the inversion temperature of the two specimens. The thermocouple junction is exposed to furnace radiation and may be a little hotter than the plate, and the difference would be influenced by the heat capacity of the plate. This is perhaps the reason for the difference between II and III, because plate III had only one-third the area of plate II. The determination on plate I is of less weight because the calibration of the thermocouple was not so accurately known.

The results as a whole are not in disagreement with the value 573° adopted in this book.

Direct temperature-time curves on powdered quartz were found unsatisfactory by Wright & Larsen as a means of determining accurately the inversion point, probably because the quantity of quartz used was too large.

The determinations just cited are the best available for fixing the exact temperature of inversion, but since nearly every property of quartz shows an abrupt change at this point, the study of the relation of any such property to the temperature will serve to determine the point. The numerical data on the various properties will be presented in later chapters, but some of the inversion-temperatures derived from them are collected in Table VII.2.

In most of these determinations the temperature was not measured with the highest available precision and accuracy, and the results are therefore not as good as those already cited. There is no special reason, however, for preferring a temperature-time curve, and it is probable that more accurate results might be obtained by the use of some other property than latent heat. A precise comparison of the inversion-points obtained with the aid of different properties might also prove of interest, not only with respect to the properties

[6] Wright, F. E., & Larsen, E. S., *Quartz as a geologic thermometer*, Amer. J Sci. (1909) **27**: 421-447; Zeitschr. anorg. Chem. (1910) **68**: 338-369.

[7] Day & Sosman, Carnegie Inst. Washington, Publ. **157** (1911).

of quartz, but also with respect to the theory of high-low polymorphism in general.

Divergent values

There are several thermal determinations of the high-low inversion point of quartz which diverge considerably from the most probable value, 573°. These may be briefly mentioned to complete the experimental record.

Stein[8] observed it by means of heating and cooling curves with a thermocouple embedded in 100 grams of quartz sand, packed down. Four determinations gave 552°, with enough absorption or release of heat to hold the temperature at that point for 25 seconds. The same value was obtained on pieces

TABLE VII.2.

DETERMINATIONS OF THE HIGH-LOW INVERSION POINT OF QUARTZ.

Observer	Property studied	Form of specimen	Inversion point	
			Rising temp.	Falling temp.
Le Chatelier (1889)...	Linear thermal expansion	Bars 5 x 5 x 110 mm	About 570	
Le Chatelier (1889)...	Rotatory power	Plate 10 x 10 x 3 mm	About 570	
Mallard & Le Chatelier (1890)	Birefringence	Plates	570	Same as rising
Wright & Larsen (1909)	Birefringence	Plates	575.5	574.4
Rinne & Kolb (1910)..	Refractive index	Crystals	569 570 571 } 571 573	Same as rising
Fenner (1913)	Latent heat	Powder	575	570
Perrier (1916)	Piezo-electricity	Plate	579	576
Bates & Phelps (1921)	Latent heat	Plates 10 x 10 x 2 mm	573.3	572.4
Perrier & Mandrot (1922)	Young's modulus	Plates	576	

of sandstone of 600 to 1000 g, containing a hole bored for the thermocouple and filled in with sand. The temperatures were measured with a platinum-platinrhodium thermocouple, presumably read with a millivoltmeter, and calibrated at the melting points of zinc, antimony, silver, and nickel.[9] The lack of details makes it difficult to judge the accuracy of this determination, but the fact that it is about 20° below most of the other measurements suggests that possibly the thermoelectric correction for atmospheric temperature was

[8] Article cited in VI, note [15].

[9] Correspondence with Professor TAMMANN (1923).

overlooked or wrongly made. The same applies to a determination made by the same author on "chalcedony" (see p. 179).

By means of a differential thermel with junctions in a crystal of quartz and a block of vitreous silica, Perrier [10] has observed the inversion point of quartz at 580°.

Perrier & Wolfers [11] used the high-low inversion of quartz to test a proposed method of detecting transformation points at which the energy-change is small. The method is a modification of the well-known differential method (see p. 84); it employs two identical specimens of the material tested instead of one specimen and a standard, and heats or cools them with a small constant time-lag between the two. A differential thermel measures their difference in temperature. When the apparent heat capacity of the substance begins to change rapidly the difference in temperature between the two specimens becomes larger or smaller than if only one specimen were being compared with a standard. The authors' application of the method to two one-centimeter cubes of quartz was rather qualitative, since one junction of the differential was not in contact with its specimen, and the inversion-temperature indicated is not at all accurate. But even if properly applied, the method seems better adapted to an inversion of type IV (see Fig. VII.1) than to an inversion of the quartz type.

Observations on the phenomena of inversion

Wright [12] describes the visible evidence of the inversion, as seen in the goniometer, in these words: "At the inversion temperature the reflection signals from all of the faces, both rhombohedron and prism, become temporarily (2 to 5 seconds) indistinct; the sharp signal widens out into a hazy patch of light, moves noticeably and finally regains its original sharpness but has usually shifted its position noticeably in the field."

Mügge [13] observed similar phenomena and studied them in detail. When a polished plane plate of low-quartz is heated to a temperature near the inversion, the reflection begins to be hazy, sometimes obscurely doubled or multiple; then two, three, or four sharper reflections appear which waver toward or away from each other or even cross one another, finally combining again into the original homogeneous clear reflection when the inversion is complete. If the temperature be held constant as near as possible to the inversion point itself, these partial reflections waver back and forth but cannot be held in place. Their direction of movement seems to bear no relation to the crystallographic directions, but their number and position do seem to be influenced by the contour of the plate.

This wavering of the plane at the inversion is much more conspicuous in thin plates than in thick. On a 0.03 mm plate it may amount to as much as 3° of arc; on a 0.1 mm plate, to 1½°; but on a plate 1 x 5 x 5 mm, to only 10′.

Rinne & Kolb [14] observed this same temporary variability of the surface

[10] Perrier, A., Arch. sci. phys. nat. (1916) (4) **41**: 492-497.
[11] Perrier, A., & Wolfers, F., Arch. sci. phys. nat. (1920) (5) **2**: 372-381.
[12] Wright, F. E., article cited.
[13] Mügge, O., article cited.
[14] Rinne, F., & Kolb, R., *Optisches zur Modifikationsänderung von α- in β-Quarz sowie von α- in β-Leucit,* Neues Jahrb. Min. etc. **1910**, II: 138-158.

reflection at the inversion point. Usually 2 reflections were visible, about 5′ of arc apart.

The permanence in position of the principal axis is shown by an experiment by Wright & Larsen[15] in which a plate parallel to the axis was observed in their thermal microscope. When placed in parallel position between crossed nicols and heated through the inversion point, the plate did not light up, showing that the optic axis did not change its position, even temporarily.

Rinne & Kolb made the important observation that the birefringence changes before the surface reflection is affected. The difference was observed by setting the crystal so that two images due to the birefringence could be observed simultaneously with each other and with a reflected image.

The change in birefringence came first and was followed after several seconds by the movement of the surface reflection. This effect was observed both with rising and with falling temperature. The lag of the surface change was a little greater with falling than with rising temperature.

The phenomena of the inversion as noted by Rinne & Kolb when measuring the indices of refraction were as follows. At the moment of the inversion the refracted images for both rays became diffuse, and moved rapidly in the field of view, becoming at once sharp again on the completion of the inversion. Faint subsidiary images were sometimes seen, however, above the inversion temperature, indicating that all parts of the crystal through which the light was passing had not inverted into exactly parallel positions. Perhaps twinning had taken place accompanied by slight displacements, or actual cracks, but since measurements were continued straight through the inversion to higher temperatures, the authors did not observe whether any such accidental changes actually occurred. After cooling again to room temperature the crystals were usually found to have been broken.

Similar phenomena are observed when the birefringence is being followed by means of the interference bands of a compensator in line with two crossed plates of quartz. At about 570° the bands become disturbed, then in a moment reappear with their original sharpness, but in a new place.[16]

The phenomena of the change in optical rotatory power are similar in kind to those just described. After increasing steadily up to the inversion temperature the rotation suddenly becomes unmeasurable because the plate of quartz becomes strongly birefringent for a few seconds. It then clears up, and the new rotatory power is found to be higher than that last measured. This phenomenon has been observed[17] within a range of temperature of 0.4°, but the actual change in the temperature of the quartz may of course be less than this,—may, in fact, be practically zero.

Le Chatelier[18] remarked the sudden and evanescent birefringence produced in a plate of quartz at the inversion point, when he was measuring the rotatory power at various temperatures. A plate $10 \times 10 \times 3$ mm showed it clearly, and the phenomenon was repeated with each rise and fall of temperature through the inversion point. In thicker plates it is much less evident.

[15] Article cited.
[16] Mallard, E., & Le Chatelier, H., Ann. Chim. et Phys. (1895) (7) 6: 90-114.
[17] Bates, F. J., personal communication.
[18] Le Chatelier, H., Compt. rend. Acad. Paris (1889) 109: 264-266.

It was also observed by Wright & Larsen,[19] who found, in measuring the rotatory power in their thermal microscope, that there was no position of total extinction while the inversion was occurring.

The temporary birefringence may be due to the large stresses set up between different parts of the plate while the quartz is inverting.

The form of the time-temperature curves observed by Bates & Phelps deserves special remark.[20] The temperature of a thermocouple inserted in the quartz plate is plotted against time, with the temperature of the furnace rising steadily but very slowly, and that of the plate rising with it. At a certain instant, coincident—where the two are both being read—with the moment when the readings of rotatory power are brought to an end by the beginning of the inversion, the temperature begins sharply to depart from its previous smooth course. After a few minutes it gradually returns to its original rate of increase. The departure thus represents an absorption of heat due to the inversion.

The interesting feature is that the temperature of the couple actually *falls* after the inversion has begun. Now it is a well-established principle that when two phases of a substance are in thermodynamic equilibrium at a fixed pressure, the temperature is absolutely constant. When a metal or a salt is heated, the temperature of a thermocouple immersed in the material rises to the melting point and remains there while melting is going on. A drop in its temperature after melting has begun means simply that it has been accidentally and temporarily heated hotter than the substance, and the true melting point is not the point where the temperature begins to depart from a smoothly rising curve, but the point to which it drops while melting is in progress.

By analogy with a melting point, the inversion point of the quartz plate would be expected to be some constant temperature toward which all the curves would fall. But the constant point in Bates' set of curves is not the minimum, but the *beginning*, which reproduces itself within $\pm 0.1°$, while the minimum varies with the rate of heating or other conditions. It reproduces itself not only when the thermocouple is inside of the crystal but even when the couple is only lying upon the surface.

Is there any other explanation for the drop in temperature, consistent with looking upon the inversion as analogous to a melting? One possibility is that when the inversion begins there is a sudden change in the relation between axial and equatorial conductivity, such that the thermocouple can be rapidly cooled by a colder part of the plate; this could be tested experimentally. Or, since quartz is very transparent to long wave-lengths beyond its absorption bands (see XXXVI), the couple may be superheated by radiant heat from the furnace, and be then pulled back by the inversion.

If we reject these explanations as unlikely, then we must admit that the inversion is not like a melting, proceeding gradually from level to level as the necessary heat is supplied, but that it spreads almost instantly through the whole crystal when once it has started, with the result that the parts which are not yet supplied with sufficient latent heat to cause the inversion to proceed directly are compelled to draw upon their heat capacity and so to become

[19] Article cited.

[20] With Dr. BATES' permission. Details will be published soon, either in a publication of the Bureau of Standards or in one of the current periodicals.

colder. This is the view that seems to be forced upon us not only by the facts brought out in Bates & Phelps' investigation[21] but also by other phenomena mentioned in this and other chapters, but before adopting so radical a view we should have further experimental evidence.

The foregoing remarks apply also to the reverse change, on cooling, except that the temperature of beginning varies within a range of 0.6° instead of 0.2°. Heat is released and the temperature of the thermocouple rises, *toward* the equilibrium-temperature if we consider melting as the true analogy, *above* the equilibrium if we consider that it is a case of forced inversion.

It is still possible to bring the idea of a forced inversion into line with the general principles already stated. It is known that stress lowers the equilibrium-temperature in such cases as melting and solution. It may be expected also to lower the inversion-temperature. When the inversion begins on the outside of the fragment the change of volume and of axial ratio in the outer portion throws the rest of the plate into a state of stress which is sometimes great enough to cause fracture. We need only suppose that this stress may so lower the inversion-temperature of the uninverted portion that its stored heat is enough to produce the inversion.[22] A lowering of several degrees would be required, however.

Taking the foregoing observations as a whole, it appears that the optical changes and the changes of dimensions may represent two different, though interdependent, happenings within the crystal. Are the thermal changes more closely allied to the optical or to the dimensional changes? An experimental study in which the refraction or rotation, the volume, and the heat absorption could all be observed simultaneously in the vicinity of 573° might yield some interesting results.

Absence of after-effects

No permanent change in any of the properties of quartz has ever been observed as a result of its passage through the high-low inversion and back again.

Rose[23] noted that a quartz crystal did not change in density by as much as 0.1 per cent as a result of heating in a procelain kiln.

Mügge[24] found that if the surface remains unbroken by cracks when the inversion is completed it retains its original reflecting power. A plane polished homogeneously-reflecting plate of low-quartz regains its quality above the inversion, and again regains it on cooling, even though the quartz may have become twinned by the reverse inversion. A plate of naturally twinned low-quartz is similarly constant in planeness.

If cracks are caused by the heating they separate such a plate into several areas of homogeneous reflection, but each such area remains unaffected by the inversion and twinning.

[21] I am quoting only their facts, not committing them to any opinion as to hypotheses.

[22] Hypothesis suggested by Dr. FENNER.

[23] ROSE, HEINRICH, article cited in IV, note [12].

[24] Article cited.

Joubert[25] found no change in rotatory power in quartz which had been heated to about 1500° and cooled to room temperature.

Historical notes on the inversion of quartz

The break-up of quartz as a result of heating to a temperature above a dull red is a phenomenon which has been known and made use of for centuries in ceramic and metallurgical processes, but it seems never to have aroused enough curiosity to lead to the discovery of the inversion, with its discontinuous change of all properties.

Pionchon[26] had recognized in 1888 that there are two distinct regions, decidedly different in character, in the curve relating the heat capacity of quartz to the temperature, but he did not suggest that there is a break in the curve, corresponding to a definite inversion point. He thought that the change from one form of curve to the other took place at about 400°.

The existence of an inversion was first announced in 1889, by Le Chatelier.[27] He was led to the discovery through noticing that the thermal dilatation of a clay containing about 15 per cent of quartz changed distinctly in character at about 600°. This peculiarity was found to be due not to the kaolin but to the quartz in the mixture. Measurements of the thermal dilatation of pure quartz then showed the existence of a sudden change of dimensions at about 570°.

The accompanying changes in other properties of quartz have subsequently been measured by various investigators, whose results will be considered in connection with the properties in question.

The designations "α-quartz" for low-quartz, and "β-quartz" for the high-modification were first applied by Mügge[28] in 1907. Subsequent confusion in the use of these terms has led to their abandonment in this book (see p. 43).

The three tridymites

Tridymite has two high-low inversions, similar to the one inversion in quartz. As the two higher-temperature modifications resemble each other more than they resemble the low-temperature modification, I have called the three, respectively, "upper high-tridymite," "lower high-tridymite," and "low-tridymite."

The low to lower-high inversion occurs with rising temperature at 117° ± 2°. With falling temperature the inversion cannot be so sharply defined, the heat-effect and optical change being spread over a range of temperature from below 117° down to about 70°, so that no sharp break can be found on a cooling-curve.

[25] Joubert, J., Journ. de Phys. (1879) **8**: 5-10.
[26] Pionchon, Compt. rend. Acad. Paris (1888) **106**: 1344-1347.
[27] Le Chatelier, H., *Sur la dilatation du quartz,* Compt. rend. Acad. Paris (1889) **108**: 1046-1049.
[28] Mügge, O., article cited.

The lower-high to upper-high inversion occurs with rising temperature t 163° ± 2°. With falling temperature this inversion, like the low to ower-high, is not sharply defined. In fact, no break is observable on the ooling-curve, although a small absorption of heat is clearly visible on the eating-curve.

Constancy of the points

Fenner [29] found the 117° inversion (low-tridymite to lower high-ridymite) to be constant within 4° for six different specimens of artificial ridymite. In addition, a determination with a thermal microscope on atural tridymite from Cerro San Cristobal gave 112°, in practical agree-ient with the determinations on artificial tridymite, in view of the much maller accuracy of this single estimate. The 117° point was also checked nder the microscope by observations on natural tridymite (Cerro San Cristobal) immersed in oil and heated by means of a copper bar.

Of the six artificial tridymite specimens referred to, three were made rom quartz at temperatures of 1000 to 1300°, and three from precipitated ilica at temperatures of 870 to 1300°. The inversion temperatures were ndependent of the source or temperature of formation of the tridymite.

Fenner found the 163° inversion (lower high-tridymite to upper high-ridymite) to be constant within 5° for the six artificial preparations of ridymite on which the 117° inversion was determined. The 163° point ould not be checked optically as there was no detectable change in the bservable refringent properties of crystals of natural tridymite (Cerro an Cristobal) immersed in oil and heated on the stage of a microscope.

Washburn & Navias [30] have confirmed the existence of the low to lower-igh inversion (rising temperature) in the region between 107 and 125°, in ie course of dilatometric experiments on tridymite made by heating purified int with sodium tungstate for 150 hours at 1300°.

Dilatometric measurements by Braesco and by Ramdohr give inversion mperatures which agree approximately with those already cited. Braesco,[31] sing a bar cut from a silica brick containing 94 per cent SiO_2 which had een largely converted to tridymite, found the first inversion at 115° and the econd at 145°, with rising temperature.

Ramdohr [32] used natural tridymite from cavities in basalt, and obtained vidence of an inversion at 144° with rising temperature, which was "strongly elayed" on cooling.

Although definite statements are made here, and elsewhere in this book, oncerning only *three* modifications of tridymite, it is possible that a fourth odification exists, above an inversion-temperature at 440°. The evidence

[29] Articles cited in IV.
[30] Washburn, E. W., & Navias, L., J. Amer. Ceram. Soc. (1922) **5**: 565-585.
[31] Article cited in IV, note [14].
[32] Ramdohr, P., article cited in IV, note [27].

for this inversion was only recently brought forward,[33] after most of the chapters of this book had been written, and it does not appear in any of the curves in the book. The evidence is dilatometric, consisting of measurements of the expansion of agglomerated bars and also of a bar cut from a tridymite brick (see p. 388), and appears entirely reliable, but the existence of an inversion at 440° should perhaps be proved optically or thermally before it is finally accepted.

Historical notes

A high-low inversion in tridymite, similar to that in quartz at 573°, was first reported by Merian[34] in 1884, but he made no measurement or estimate of the temperature. He observed with a polarizing microscope a small plate of tridymite which was heated by a small blast flame, and observed "on moderate heating" that it lost its birefringence and became completely isotropic. The phenomenon reversed itself on cooling, and was caused to repeat several times with longer periods of heating between.

Mallard[35] (1890) placed the inversion at 130° ± 5°, but does not state how this temperature was determined. He observed the break-up of the lower high-modification, on cooling, into several differently oriented areas of low-modification. He could observe no other inversion at any temperature up to a red heat.

Fenner[36] was the first to observe that there are two inversions, one at 117° and one at 163°, thus dividing what was formerly called the β or high-temperature modification into two, which he named β_1 and β_2, and which I have called the "lower high" and the "upper high" because of the confusion in the use of the Greek-letter designations. The higher inversion does not show optically, so it was not found by Mallard.

The cristobalites

Like quartz and tridymite, cristobalite has a high-low reversible inversion, which occurs at a temperature between 200° and 300°. This inversion, however, stands in a class by itself in comparison with other known polymorphous inversions, in that its temperature varies widely according to the previous history of the crystal.

Two important features of this previous history have been recognized as influencing the inversion temperature:

(1) The temperature at which the cristobalite was originally formed or at which it has been brought to equilibrium.
(2) The kind of silica from which the cristobalite was originally formed.

[33] Goloubinoff, V. de, *Contribution à l'étude de briques silice,* Thèsis, Nancy, 1925, 49 pp. Travers & Goloubinoff, Rev. de Metall. (1926) 23: 27-47, 100-117.
[34] Merian, A., *Beobachtungen am Tridymit,* Neues Jahrb. Min. etc. 1884, I: 193-195.
[35] Article cited in V, note [18].
[36] Articles cited in IV.

Bearing in mind these two complications, we must also remember that ristobalite, of whatever origin, resembles tridymite and other substances chibiting high-low polymorphism in giving a different temperature of nversion according to whether it is being heated or cooled. This difference ay be fairly large.

Finally, there is a difficulty about the very definition of the "inversion mperature," because the properties seem not to change suddenly at a rtain temperature as with quartz, but only to change *rapidly* through a *nge* of temperature. The inversion may thus superficially appear to long to type IV (see p. 113).

Type of the inversion

The experimental data are not yet adequate to decide to what type the ristobalite inversion really belongs. The crystals usually dealt with are ther very small, or break up into very small units in passing through e inversion. We are therefore measuring the properties of an *aggre-te,* and this fact has a good deal to do with the validity of our conclusions.

For simplicity, consider a single small crystal of cristobalite at a tem-erature above the inversion, and suppose it to be cooling down while we easure its volume from time to time. After passing through the inver-on the crystal is found to have decreased in volume and to be birefringent. here must have been, therefore, a change of symmetry, and therefore e inversion of the crystal cannot be of type IV. It may be of type I, , or III, and the form of its volume-temperature curve, if we could etermine it, would show to which one of these it belongs.

Now suppose another cristobalite crystal placed alongside the first, and ppose that we are measuring the total volume of the pair. The inversion-mperature of cristobalite can vary, and this second crystal may have a fferent inversion-temperature from the first. The more rapidly curving rts of the volume curves of the two may overlap and the volume curve the pair will then resemble neither I, II, nor III. Add many more ystals, having slightly different inversion-temperatures, and the volume rve of the aggregate, smoothed out by our crude methods of measure-ent, may look like a curve of type IV, and yet be really made up of many verlapping curves of types I, II, or III.[37]

ariation of the inversion-temperature with the temperature of formation

The inversion of cristobalite formed at a high temperature comes *gher* than the inversion of cristobalite formed at a lower temperature.

[37] Since this was written, Weil (Compt. rend. Acad. Paris (1926) **182**: 1165-67) has published observations made with the polarizing microscope on cristobalite gregates which were heated or cooled very slowly. He finds that the inversion curs at different points in the aggregate at different temperatures, although the version-temperature at a given spot and for a given direction of temperature-ange is constant within 2°.

The range of inversion points with rising temperature has been found [38] on more than 30 specimens to be from 220° as a minimum to 277° as a maximum, a range of 57°. The range with falling temperature, on the same specimens, was from 198° as a minimum to 241°, a range of 43°.

Experiments show that it is not fundamentally the temperature of formation that determines the inversion-temperature, but the temperature at which the cristobalite has been heated long enough to realize an approach to equilibrium. Thus, when the cristobalite formed at the lower temperature and possessing the low inversion-point is heated for some time at

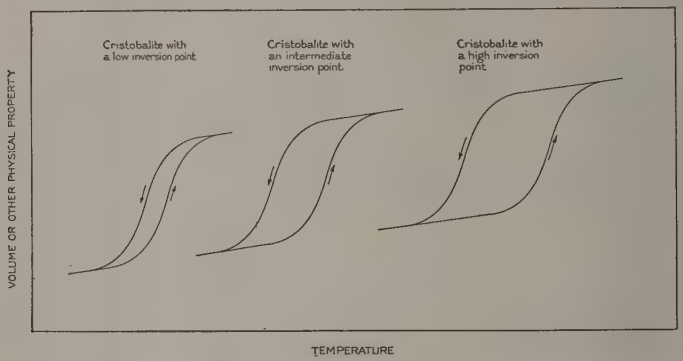

Cristobalite with a low inversion point
Cristobalite with an intermediate inversion point
Cristobalite with a high inversion point
VOLUME OR OTHER PHYSICAL PROPERTY
TEMPERATURE

FIG. VII.2.—Diagram to illustrate the principal two kinds of variability in the high-low inversion of cristobalite.

1500 to 1600°, the high-low inversion-point is found to have risen; and vice versa.

The temperature-hysteresis and its variability

As already remarked, cristobalite resembles tridymite and other substances exhibiting high-low polymorphism in giving a different temperature of inversion according to whether it is being heated or cooled. This difference, or "temperature-hysteresis," in cristobalite was found by Fenner to be from 16 to 42°.

The temperature-hysteresis is not constant, but varies from specimen to specimen. In general, the higher the inversion-point, the wider the difference between the inversions on heating and on cooling.

This rather confusing behavior may be made clearer by reference to the curves of Figure VII.2.

[38] FENNER, articles cited.

Variation of the inversion-point with the source of the cristobalite

It is quite clear that there is a change of inversion-point with the temperature at which the cristobalite was formed or to which it has been heated. Another source of variation also exists, but can not be so well defined quantitatively; this is the variation according to the different materials from which the cristobalite was made. With the same temperature of formation, cristobalite made from amorphous silica (either vitreous or precipitated silica) has a higher inversion point than cristobalite made from quartz. (Fenner.)

These variations in the inversion-point of cristobalite probably correspond to real variations in the internal structure or constitution of the substance.

There are noticeable differences among the shapes of the volume-change curves of Rieke & Endell [39] for cristobalite from Norway quartz, vein-quartz, flint, and amorphous silica, indicating that the source from which the cristobalite was derived does affect the inversion phenomena. The curves are only qualitative and no exact quantitative deductions can be made. It is noticeable, however, that the cristobalite from flint shows a narrower range of temperature within which the volume-change occurs than do the cristobalites from pegmatite quartz, vein-quartz, or precipitated amorphous silica.

Washburn & Navias [40] found that cristobalite made by heating chalcedony (from Yellowstone Park) for 2 hours at 1430-1460° had a falling-temperature inversion-point of 220°, while cristobalite made by heating black French flint under similar conditions had a falling-temperature inversion-point of 227°. Better-crystallized cristobalite, made by heating calcined flint with sodium tungstate for 7 hours at 1500°, had an inversion-point of 244°. While not large, these differences may represent a real difference in inherited structure.

Both the dilatometer curves and the time-temperature curves made by Washburn & Navias indicate that the inversion of an aggregate of cristobalite crystals is either of type III or of type IV. The same is indicated by Rieke & Endell's dilatometer curves.[41] A similar dilatometer curve by Endell [42] looks more like type IIa. But it should be noted that all of these are *time* curves; in such curves, temperature gradients and the flow of heat through the material tested may smooth out breaks which might be quite sharp if measured on a single crystal.

Phenomena of the inversion

The inversion at 200-275° is rendered easily visible, when the temperature is falling, by the change in transparency of the cristobalite. It becomes suddenly opaque or milky white at the inversion-point, because of the breaking up of the original homogeneous fragment into a great

[39] Rieke & Endell, article cited in V, note [14].
[40] Article cited in note [39].
[41] Pp. 71-72 of article cited.
[42] Endell, p. 1856 of article cited in V, note [41].

TABLE VII.3.

EFFECTS OF TEMPERATURE OF FORMATION AND OF ORIGINAL SOURCE UPON THE INVERSION-TEMPERATURE OF CRISTOBALITE. FENNER.

Specimen No.	Original form	Method of preparation	Temperature of formation	Inversion-temperature		Difference
				Rising	Falling	
134	Fine ground quartz	Dry heating	Ab. 1700	259.9	232.3	27.6
179	Do	Gas furnace, 40 min.	1640	268.2	240.5	27.7
116b	Large quartz crystal	Dry heating	1600	264.8 263.5	233.2 233.7	
				264.1	233.4	30.7
108	Fine ground quartz	Na_2WO_4 flux	1580	272.1 273.6		
				272.8	238.5	34.3
111	Do	Do	1570	274.5 272.5 276.9		
				274.6	238.1	36.5
124	Do	No flux	1580	261.7 260.8 261.6	231.4 232.8	
				261.4	232.1	29.3
160a	Do	No flux	1580	259.9 262.6	231.5 229.3	
				261.3	230.4	30.9
126	Do		1510	248.0	224.5	23.5
121	Do		1470	240.1	218.8	21.3
133	Do	Heated 66 hrs.	1300–1400	232.5	209.2	23.3
184	Do	Heated 90½ hrs.	1360	229.5 229.1	213.8 212.9	
				229.3	213.3	16.0
168	Tridymite	Dry heating	Ab. 1580	268.3	238.2	30.1
158a	Cristobalite, fine	Na_2WO_4,* blast-lamp	?	272.1 272.0	231.9 233.5	
				272.0	232.7	39.3
116a	Vitreous SiO_2	Dry heating	1600	271.1	234.3	36.8
183	Do	Heated 93 hrs.	1360	258.5 255.1 257.0	218.5 217.2	
				256.9	217.8	39.1
166a	Do	Heated 68 hrs.	1025–1075	219.7	198.1	21.6
125	Amorphous precipitated SiO_2	Dry heating	1450	258.5	229.1	29.4
142	Do	Heated 70 hrs.	Ab. 1100	230.8	207.2	23.6
175	Do	Heated 69 hrs.	Ab. 1030	225.1	205.1	20.0

* Product is a mixture of tridymite and cristobalite.

many small fragments. This break-up cannot be due to the volume change alone, for the similar inversion in quartz at 573° may occur without producing a single crack, although the volume change is fairly large.

TABLE VII.4.

INVERSION-POINTS OF CRISTOBALITE, AS OBSERVED BY VARIOUS INVESTIGATORS.

Observer	Source	Property studied	Inversion-point	
			Rising	Falling
Mallard (1890)	Natural, Mexico	Birefringence	175	175
Le Chatelier (1890)...	From agate(?) at 1500°	Dilatation	210	
Wright (1911)**.....	Spherulites in glass	Birefringence	Ab. 225	
Fenner (1912)	See VII	Latent heat	220 (min)	198 (min)
Endell & Rieke (1912).		" "	230	
Endell & Rieke (1912).	Dinas brick	" "	....	226–229
Rieke & Endell (1913).	" "			228
	Norway quartz	Volume	210–245 †	220–200 *
	Flint	"	228–230 †	229–226 *
	Amorphous SiO_2	"	215–250 †	217–208 *
	Vein quartz	"	....	223–205 *
Rieke & Endell.....	Vitreous SiO_2 at 1500°, 1 hr.	Cracking (milkiness)		229
Ramdohr (1920)	Basalt, Blaue Kuppe	Not stated	235–250	215–230
Wietzel (1921)	Pptd. SiO_2 at 1600°	Heat capacity	270	230
	" " " 1100°	" "	230	200
Washburn & Navias (1922)	Chalcedony at 1450°	Latent heat		220
	Flint " "	" "		227
	Purified flint at 1500°	" "		244

* Temperature of dilatometer probably lower than specimen.
† Temperature of dilatometer probably higher than specimen.
** SHEPHERD & RANKIN, J. Ind. Eng. Chem. (1911) 3: p. 223.

The break-up of cristobalite is probably connected with the change in symmetry from isometric to orthorhombic, this change involving differences in contraction along the three mutually perpendicular axes of low-cristobalite. If the newly formed units then happen to be differently oriented, differential contraction will produce sudden stresses and will rupture the original fragment.

Experimental data on the inversion-temperatures of cristobalite

Fenner's experiments furnish the principal source of information on the inversion-temperatures of cristobalite. His data are given in Table VII.3.

Isolated measurements of inversion-temperature have been made by other observers in connection with studies of the specific volume, heat capacity, dilatation, and other properties. Some of these measurements are assembled in Table VII.4.

Suggested causes of the variability of the inversion-point

Several possible causes for variation in the inversion-point, aside from a real difference in structure or constitution, suggest themselves and deserve theoretical and experimental consideration. These are:

(1) Impurities in solid solution in the silica. This possible cause was shown by Fenner to be non-existent. Cristobalite made from purest selected quartz without the aid of a flux, and containing only 0.04 to 0.07 per cent impurities, showed the same variations as other kinds of cristobalite.

(2) Time lag in the inversion. This possible cause also proves to be non-existent. With a given sample of cristobalite, the inversion with rising temperature occurs at the same temperature whether the rate of heating be fast or slow. Holding the sample at a temperature near the inversion-point also produces no effect. "Seeding" the sample by inverting a small portion of it locally with a hot platinum wire is likewise without effect.

A very slow rate of cooling, similarly, has no effect on the inversion-point with falling temperature; it is the same as when the cooling is rapid.

(3) Variation in fineness of grains. The melting-point, solubility, and in general all the properties concerned with heterogeneous equilibrium, are affected by the size of the grains of a finely powdered substance (see IX). It is natural to expect that the high-low inversion-point will be affected also. Experiments by Fenner showed that grinding the powder until the grains were so small as to be almost beyond the resolving power of a Fuess No. 9 objective (about 0.7 μ) lowered the point (as determined with rising temperature) only 2°. The effect on the falling-temperature point was larger, amounting to a lowering of 12°. With another preparation fine grinding *raised* the rising-temperature point 5° and lowered the falling-temperature point by the same amount.

It is not certain how much of this apparent change in the inversion-point is real. Since the determinations were made by means of a temperature-time curve with a differential thermel, a change in the thermal conductivity of the charge of silica might produce an apparent change in the point. This needs to be further studied by comparison of the thermal method with dilatometric, optical, and other methods of determination.

It is evident, however, that fineness of grain alone will not account for the differences of 43 to 57° which follow different temperatures of formation.

(4) Variation in the size of the twinned regions in low-cristobalite. In passing from the state of isometric high-cristobalite to that of birefringent low-cristobalite, each crystal becomes divided up into twinned portions. If the size of these portions varied greatly from one preparation to another, it is conceivable that the inversion-point might be affected just as by fine grinding.

The only way in which this possibility has been tested experimentally has been by the study of the effect of great variations in the rate of cooling a given charge through its inversion-temperature, the inversion-point being determined afterwards in the usual way. Fenner found that a charge heated at 416° to 377° and then quenched by plunging it into cold water gave the same inversion-point, within 1°, as a charge heated at 286° and then cooled very slowly through the inversion (3 hours from 280° to 229°).

Further notes on the experimental data

Endell & Rieke [43] state that the rate of inversion of cristobalite at the high-low inversion-point, as observed in clear pieces of vitreous silica which have been crystallized by heating at 1450° or above, is about 1 cm per minute. This probably represents nothing more than the rate at which the temperature of inversion was reached at successive points in the fragment while it cooled irregularly in the air. Without further study it can not be taken to represent a true rate of inversion at constant temperature.

Endell [44] stated in 1912 that he had found the low-to-high inversion of cristobalite to be reversible with difficulty, and that rapid cooling after the crystals had been heated to above 220° left them in the isotropic high-form, from which the change at atmospheric temperature was a matter of some hours.

Schwarz [45] has also stated that cristobalite after being heated about 15 minutes at 250° and then quickly cooled remains isotropic.

These statements are in such direct contradiction to the numerous observations of all other investigators that it can hardly be admitted without further evidence that the phenomena observed were really due to a delayed inversion. It is easy to be mistaken on this point because cristobalite after passing through the inversion is very fine grained, and its birefringence, furthermore, is small, so that it may give a false appearance of being isotropic.

In determining the inversion-temperature of cristobalite from several different sources, Endell & Rieke noted that the sharpest thermal effect (on cooling) was obtained with cristobalite from fused silica brick. They ascribe this sharpness to the accelerating effect of the slight impurities which are thoroughly disseminated in such cristobalite. This is only a surmise, not proved by tests, although the impurities may possibly have something to do with the sharpness of the inversion-point.

Historical notes on the high-low inversion of cristobalite

A high-low inversion in cristobalite similar to those in quartz and in tridymite was first reported for cristobalite by Mallard [46] in 1890. Heating it under oil, he estimated the inversion-point to be at 175°. This determina-

[43] Article cited in VI, note [41].
[44] Endell, K., *Ueber die Konstitution der Dinassteine*, Stahl u. Eisen (1912) **32**: 392-397, pl. 8.
[45] Article cited in IV, note [20].
[46] Article cited in IV, note [18].

tion was probably in error, as no subsequent determinations have placed it so low. The extreme range of values, inclusive of the temperature-hysteresis, as found by later investigators is 198 to 277°.

The unusual feature of variation of the inversion-point with previous history of the crystal was discovered by Fenner in 1912. He made the first accurate measurements of the inversion-temperature, by using a differential copper-constantan thermel, and soon found variations between different specimens which were far outside the possibilities of error in the method. Further study brought out the essential variability in the inversion itself, already referred to in the preceding pages.

Chapter VIII. COMPLEX PHASES

In the preceding chapters we have considered the relations between homogeneous distinct forms or phases of silica having definite and reproducible properties. Now silica is such an extraordinarily sluggish substance in its transformations from one form to another that the question is pertinent whether it may not be possible to alter slightly the structure of one of these forms and obtain thereby a modification or *complex phase* of silica which is slightly but permanently different from the principal forms.

In most substances the atoms are too mobile to permit such modifications to exist for more than a very brief time, but in silica there is reason to believe that they do sometimes persist indefinitely. Cristobalite itself, with its variable high-low inversion-point, is perhaps a form of this kind. Three other aberrant phases which have attracted some attention may also be considered as complex phases derived from the principal forms; they are:

(1) Optically anomalous quartz,
(2) Vitreous silica with crystalline properties,
(3) Amorphous silica with crystalline properties.

Optically anomalous quartz

The grains of quartz in many igneous, metamorphic and sedimentary rocks exhibit so-called "optical anomalies," which will now be briefly described.

When a plate or section of homogeneous quartz, cut parallel to the crystallographic axis, is viewed between crossed nicol prisms in the polarizing microscope, it lights up and darkens alternately four times when the microscope stage makes one complete revolution. At any moment the light or darkness is the same in all parts of the section. But if the quartz is of the special kind considered in this chapter, it does not light up or darken uniformly, but the light sweeps across it like the waves in a field of grain under a summer breeze; it shows *undulatory extinction.* It acts as if the direction of the optic axis changed progressively from point to point.

Seen in a section perpendicular to the apparent crystallographic axis, such quartz gives colors and interference figures characteristic of biaxial substances, although homogeneous quartz is known to be uniaxial (see XXX).

These features of undulatory extinction and biaxiality have often been ascribed to strain, because similar optical effects can be produced in an

isotropic substance such as annealed glass by a mechanical stress (see XXXIX). Such effects are temporary and reversible, disappearing when the stress is removed. The stress may be due to non-uniform cooling from the soft state, as in a Prince Rupert drop, and here, again, the evidences of strain disappear almost completely when the drop explodes into small fragments.

The supposed strain in quartz, however, is not reversible in this way. The undulatory extinction still persists, even though the quartz be ground to a very thin section or crushed into very small fragments. It is evidently due, then, to a real variation in internal structure. The variation may have been caused by a mechanical stress in the first place, as is indicated by the fact that it is most commonly found in the quartz of dynamically metamorphosed rocks, but whatever its original cause it does not now represent the effect of a mechanical stress, as we ordinarily understand that expression.

The experimental data

The most thorough study of optically anomalous quartz is that by Wyrouboff in 1886, but important contributions have also been made by Breithaupt, Reusch, Böklen, Brauns and others. The data relate almost entirely to the refractive properties of the specimens and the optical effects resulting therefrom, and cannot very well be taken up in detail at this point.

No clear statement of the anomalies in terms of the general principles of crystal optics has as yet come out of these researches. The view that they represent true variations of structure has recently received strong support from optical and X-ray investigations on garnet by Rinne,[1] who shows that the anomalies are best explained as due to systematic displacements of electron orbits caused by minute abnormalities in the building up of the crystal from its atoms.

Transformations of anomalous quartz

Sidorenko[2] found that the small degree of biaxiality ($2E = 3\frac{1}{2}°$) observed by him in optically anomalous amethyst disappeared permanently when the specimen was heated in a blast-lamp flame.

A crystal of quartz showing undulatory extinction, which we may, for brevity, call "undulatory quartz," behaves rather differently from homogeneous quartz at the high-low inversion, according to Holmquist.[3] He found that undulatory quartz was broken into a great number of very small fragments by the inversion at 573°, while his specimens of homogeneous quartz were not.

Observations by Holmquist and by Endell & Rieke[4] show also that undulatory quartz breaks up into very fine fragments when heated to a temperature of 1200° or higher, where the inversion to cristobalite begins.

[1] Rinne, F., Centralbl. Mineral. 1925, A: 225-241.
[2] Sidorenko, M., Mem. New Russian Soc. Naturalists (Odessa) (1890) **15**, II: 41-58 (Russian).
[3] Article cited in V, note [9].
[4] Article cited in V, note [15].

Vitreous silica with crystalline properties

Some specimens of vitreous silica are found to be irregularly birefringent, in a way which shows that the birefringence is not due to strain but to some property of the glass itself. The birefringence is very small, about one-sixtieth of that of quartz, but it persists when the glass is softened and drawn or blown. By proper heat treatment it can be made to disappear and then reappear. These phenomena have never been observed in ordinary silicate glasses, in which birefringence has always been found to be due to strain.

Fig. VIII.1.

Fig. VIII.2.

Fig. VIII.1.—Granular birefringent structure in a disk of vitreous silica. Magnified 2 diameters. (Rayleigh, 1921.)

Fig. VIII.2.—Birefringent structure in vitreous silica, drawn out into ribbons. (Rayleigh, 1921.)

In a mass of vitreous silica made by the fusion of quartz crystals the birefringent structure may consist of grains about ½ mm in diameter, oriented at random, as in Figure VIII.1. If this grained glass is softened in a flame and drawn out, the grains become elongated into fibers or ribbons, as in Figure VIII.2. All of these fibers show parallel extinction (see p. 639). Their length is parallel to one of the axes of the optical ellipsoid (see p. 585), but not always the same axis.

The granular birefringent structure in Figure VIII.1 is seen to be not uniform but somewhat irregularly distributed. This light and shade effect is due to true strains in the glass which cause a general variation of birefringence, superposed upon the granular structure. This general or regional effect can be varied, either temporarily by the application of screw

pressure to the disk, or permanently by heating the disk to a yellow heat in the oxy-gas flame, which introduces new strains on cooling. The granular structure is rendered more distinct by moderate strains, as Rayleigh showed theoretically that it should be. The disk photographed is 2.5 mm thick, so that there is some overlapping and confusion of the granular structure.

The experimental data

The birefringence of vitreous silica was first noticed by Rayleigh in casual observations made to test the suitability of the glass for windows in apparatus for the measurement of the scattering of light by gases. Our

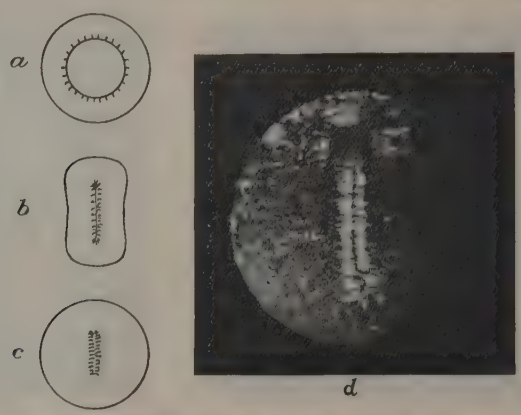


FIG. VIII.3.—Birefringent ribbons in vitreous silica rod and tubing.
(*a*) Ribbons lining a tube.
(*b*) Effect of collapsing the tube (*a*).
(*c*) "Caterpillar structure" observed by Rayleigh in a silica rod.
(*d*) Photograph of cross-section of silica rod containing caterpillar structure. Crossed nicols, length of caterpillar placed at an angle of 45° to planes of nicols.

present knowledge of this peculiar kind of glass comes mainly from his experiments.[6]

The birefringence being very small, it is necessary to have a completely dark field between the nicol prisms used for polarizer and analyzer. To this end it is desirable to dispense with lenses and protective glass covers, or if glass must be used, to have it thin and free from strains. Large nicol prisms are desirable. The effects cannot be obtained with the ordinary polarizing microscope as used in petrologic work.

As already remarked, the granular structure can be drawn out into ribbons if the glass is softened in a flame, as is shown in Figure VIII.2, but better

[6] RAYLEIGH (IV), *Double refraction and crystalline structure of silica glass*, Proc. Roy. Soc. London (1921) (A) **98**: 284-296, pls. 7-9. Preliminary announcement in Nature (1919) **104**: 153.

specimens for the study of these ribbons can be obtained from commercial silica rod and tubing. In silica rod the ribbons are perfectly straight and parallel to the length of the rod.

The maximum cross-section of the ribbons observed by Rayleigh in a rod about 1 cm in diameter was about 0.5 mm broad × 0.1 mm thick, but the breadth was usually about 0.13 mm. Narrower ones were also seen down to the limit of visibility. They persisted in thinner rods, down to 0.4 mm in diameter, and also in a very thin freshly drawn rod of high strength, of the kind described by Griffith (see p. 485).

Some silica tubes were found to be lined with the birefringent ribbons, with their breadth along the radius of the tube, as indicated in Figure VIII. 3(a). It is easily seen that if such a tube were to be collapsed to make a rod, the arrangement of ribbons would be as in Figure VIII. 3(b). This is apparently the origin of the "caterpillar structure" found by Rayleigh in a 1-cm rod, as shown in the cross-sections in parts (c) and (d). The section cuts perpendicularly across a row of fine capillary tubular streaks, whose cross-sections make a row of very small dots down the middle line of the caterpillar. The dimensions of the caterpillar were about 1 × 6 mm, with an isotropic portion about 0.1 mm wide down the middle.

Rayleigh also measured the birefringence of the ribbons. In general, if one of the ribbons be regarded as a rectangular crystal, the extinction is parallel on all its faces.

Lengthwise of the caterpillar and also lengthwise of the ribbons themselves the birefringence reinforces that of a quartz wedge cut parallel to the axis, and placed parallel to the ribbon and to the caterpillar, respectively. In these two directions the relative retardation was found to be the same, as nearly as it could be measured (about 5 to 10 per cent), and amounted to 0.029 wave-length per mm thickness. This is about one-sixtieth of the value for quartz perpendicular to its axis. In the third direction sufficient thickness was not obtainable to measure the birefringence, but the vibration-direction of greater index was found perpendicular to that in the other azimuth of the ribbon.

In another specimen, however, the vibration-direction of greater index was the same in both azimuths around the ribbon.

From Rayleigh's optical data the optical character of the ribbons can be deduced.[8] In his principal specimen (the one containing the caterpillar) the ribbons act as negative biaxial (but nearly uniaxial) crystals, whose elongation is positive if seen flatwise, or negative, if seen edgewise. Without quantitative measurements the second specimen cannot be exactly described, but from Rayleigh's notes it would seem to come nearest to an optically negative, negatively elongated crystal. (The meaning of these optical constants and optical characters will be more fully described in Chapters XXX and XXXII.)

These ribbons come nearer answering the description of Lacroix's "pseudo-chalcedonite" than they do to any other of the micro-crystalline fibrous forms of silica (see X).

The ribbons flow with the glass when the glass is softened in a flame and

[8] I am indebted to Dr. F. E. Wright of the Geophysical Laboratory for a confirmation of this analysis.

is drawn, bent, or twisted. When such ribbons are examined in polarized light, the extinction is found to be tangent to the curvature of the ribbon at every point. The direction of extinction follows the sinuosities of the ribbon, even around a right-angled bend in a rod.

Similar fibrous birefringence was observed by Rayleigh in a vitreous silica crucible cover, the pattern of fibers showing clearly how the cover had been made from a bulb blown on a tube.

Disappearance and reappearance of birefringence

The most interesting phenomena of the birefringent glass are the effects produced by heating at various temperatures. A small piece of the sheet glass was photographed, and then was heated to a white heat in the oxy-gas flame, avoiding mechanical deformation while the piece was soft. It was photographed again when cold. When one photograph was reversed and placed edge to edge with the other, a considerable degree of symmetry was evident between the two, showing that much of the original structure had survived the heating.

Not all of it survives, however. Apparent contraction of some of the grains occurred after several minutes at about 1000°. Furthermore, the glass lying between the ribbons in commercial rod is quite free from birefringence, showing that parts of the glass have become wholly isotropic before or during the making of the rod.

Rayleigh was not able to destroy the ribbons in a rod even by fusion at the highest temperature of an oxy-gas flame. In built-up optical vitreous silica, however, the granular birefringent structures could be made to disappear, and some interesting phenomena of their removal and reappearance were observed. A birefringent ring structure, shown by various methods to be due to stress and not to crystallinity, was also involved.

A silica disk was cut into two thinner disks each about 1 mm thick. The results of the experiments upon these two may be summarized as follows:

Disk	Treatment	Result
Nos. 1 & 2	Heated in Meker furnace at about 1000° for 2 hrs. Quenched in water.	Birefringent structures disappeared.
No. 1	Heated as above for 10 min.	Both structures reappeared.
No. 2	Heated as above for short intervals:	
	5 min. total	Distinct reappearance of structure.
	20 min. total	Maximum redevelopment of structure.
	60 min. total	Structures nearly all disappeared again.

A partial explanation of this puzzling behavior will be offered in Chapter XVI.

Other observations of birefringent vitreous silica

In 1907 Mügge[7] observed that vitreous silica, fused by wrapping half of a plate of quartz in platinum and heating the exposed half in an oxy-gas flame, was not isotropic but showed a weak birefringence in the aggregate. He ascribed the effect to microscopic unfused splinters of quartz included in the glass, but did not actually observe any such splinters. He probably had the same birefringent glass that Rayleigh afterwards studied.

Lawson[8] has recently recorded an observation made a number of years ago, which is of interest in connection with this subject. It is known that crystalline quartz is colored yellow-brown or brown-red by the radiation from radioactive substances, sometimes uniformly, sometimes in streaks. Vitreous silica is usually colored a uniform brown-violet by similar radiations. Lawson recalls the occurrence of spiral streaks of dark violet in a vitreous silica dish used by Hönigschmidt in 1911 for the recrystallization of radium chloride. No color appeared between these streaks, which extended almost to the rim. When the glass was heated in a Bunsen flame the color disappeared with the production of a brilliant blue-violet luminescence.

This decided difference in coloring under the action of radium indicates a difference in constitution between the colored and colorless streaks of the dish, which may be of the same character as the crystalline and non-crystalline ribbons in the glass examined by Rayleigh.

Amorphous silica showing birefringence

Anhydrous silica bearing optical evidences of crystallinity is obtainable by the extraction of the basic oxides from certain silicates and subsequent dehydration of the hydrated silica so obtained. Such varieties of silica usually retain the external crystalline form of the parent mineral,—in other words, are artificial pseudomorphs.

These varieties furnish additional evidence of the great disinclination of the atoms in silica to undergo rearrangements, a phenomenon repeatedly referred to in Chapters IV and V.

Experimental data

Many experiments on the extraction of bases from silicates are to be found in the literature. Only a few typical cases need be quoted here.

Gorgeu[9] observed that when crystals of artificial fayalite, $2FeO.SiO_2$, which had been heated at a bright red until the iron was oxidized to the ferric state, were digested with concentrated boiling hydrochloric acid, the iron was entirely removed leaving pure silica which retained the form of the original fayalite crystals. This silica, when saturated with water, was isotropic, but

[7] Mügge, O., article cited in VII.

[8] Lawson, R. W., *The doubly refracting structure of silica glass,* Nature (1919) **104**: 335.

[9] Gorgeu, A., *Sur une pseudomorphe artificielle de la silice,* Compt. rend. Acad. Paris (1884) **98**: 1281-1282.

acted like a birefringent substance when dried in air, when it still retained 4 to 6 per cent of water.

A similar product was obtained by Gorgeu [10] from artificial knebelite (23 per cent MnO, 47 per cent FeO) presumably oxidized and treated with acid as above; and also direct from artificial fayalite by digestion for a long time with hydrochloric acid.

Tephroite, rhodonite, hypersthene, diallage, and hornblende were not completely oxidized by treatment similar to the above, and did not yield silica pseudomorphs.

E. Bertrand [11] concluded, after examining this pseudomorphous silica, that it is neither crystalline nor truly birefringent, and that its action on polarized light is the action which would be produced by very acute-angled prisms of any transparent isotropic substance in air. When surrounded with water, whose index is nearer to that of silica than to that of air, this prismatic effect tends to disappear.

Rinne [12] found that a pure silica pseudomorph after heulandite ($CaO.Al_2O_3.6SiO_2.6H_2O$) could be obtained by treating this mineral with dilute sulfuric acid or concentrated hydrochloric acid until the lime and alumina were removed, and then heating the residue over the blast flame to remove all water.

The product retains the form of the original cleavage flakes of heulandite, parallel to (010), from which it is prepared. It is optically biaxial, with small optic axial angle. The value of the optic axial angle varies in different regions of the plate. The first bisectrix is perpendicular to the plate. The substance is optically negative, and fairly strongly birefringent.

Its specific gravity, determined by weighing about 5 g under water, is 2.143. It does not become uniaxial on heating up to 400°, but on the contrary becomes somewhat more birefringent. It is therefore neither tridymite nor cristobalite. Heating to a glowing red in a Bunsen flame causes a distinct permanent increase in the birefringence.

Schaller and Larsen [13] prepared a hydrated pseudomorph containing only SiO_2 and H_2O by treating gillespite, $BaO.FeO.4SiO_2$, with acids. The original mineral is uniaxial negative, the hydrated pseudomorph is also uniaxial negative, and the pseudomorph after dehydration at a red heat is still uniaxial negative. An X-ray picture [14] of the last product shows a faint pattern of a few lines.

A birefringent residue containing only silica and water was produced by Morey [15] by treating crystals of $K_2O.H_2O.4SiO_2$ with dilute hydrochloric acid, and similar hydrated products have been studied chemically by Tschermak and others. We are interested here only in the persistence of the birefringence in the dehydrated silica, and in the explanation of this peculiarity. The explanation is not yet clear.

[10] Gorgeu, A., *Sur plusieurs productions artificielles de minéraux naturels obtenus a l'aide des chlorures metalliques*, Ann. Chim. et Phys. (1885) (6) **4**: 515-561, p. 542.

[11] Gorgeu, article cited (1884).

[12] Rinne, F., *Ueber die physikalisch-chemische Einwirkung von Schwefelsäure und Salzsäure auf Heulandit und über ein leicht zu gewinnendes, krystallisirtes Siliciumdioxyd*, Neues Jahrb. Min. etc. 1896, I: 139-148.

[13] Personal communication.

[14] By Dr. Posnjak.

[15] Morey, G. W., J. Amer. Chem. Soc. (1914) **36**: p. 222.

Chapter IX. EFFECTS OF SUBDIVISION AND TWINNING

General effect of fine subdivision

When a portion of matter is mechanically subdivided a certain amount of work must be done against the cohesion between the atoms or between the molecules in order to separate the fragments. If the fragments are large compared to the size of an atom, the amount of work per atom is negligibly small. But if the subdivision is continued to smaller and smaller fragments, a size will soon be reached which contains so few atoms that the average work per gram-atom of again subdividing the piece is an appreciable fraction of the possible energy changes which can be brought about in the substance.

A gram of a substance in a state of very fine subdivision may thus possess a greater zeta or free energy (see p. 47) than a gram of the same substance in one homogeneous piece. Any properties involving energy or entropy must therefore be changed. The vapor pressure and solubility of the fine powder are greater, its melting point is lower, its heat capacity greater, etc.

Very fine subdivision must therefore be expected to change the temperatures of equilibrium stated in Chapters IV to VI. Few quantitative data are available, but such as we have indicate that the effect of fine subdivision of silica is usually not large—of the order of 10°C or less.

It should be noted that the finely divided phase is metastable with respect to the coarse phase. Very fine drops of liquid, since they have a higher vapor pressure than large drops, evaporate, and the material is redeposited on the large drops. Very fine crystals in contact with a solution, since they have a greater solubility than coarse crystals, dissolve, and the material is then redeposited on the larger crystals.

The preceding remarks have all had reference to subdivision by mechanical means. But in crystalline substances we may have another manner of subdivision, arising from *twinning*.

Effect of twinning

Reference will be made in a subsequent chapter (XII) to the types of twinning shown by the modifications of silica. For the present, we are concerned only with the general effects of the phenomenon on the classification of the phases and the temperatures and rates of transformation.

As long as the twinning is on a large scale in comparison with atomic sizes, the properties of the substance are not appreciably influenced. But when the twinning becomes microscopic or submicroscopic, the effect of

the size of each homogeneous portion on its physico-chemical properties must be considered, just as when it is finely subdivided mechanically.

Reasons can be brought forward for treating submicroscopically twinned crystalline material as a separate phase. No obvious break in the properties can be seen at the so-called composition-surface separating two reversed parts of the twinned crystal. The distance from an atom on one side of this boundary to one on the other side may be of the same order of magnitude as the distance between atoms in the truly homogeneous part.

But as the twinning is made finer and finer it will ultimately reach atomic dimensions, and it is logically possible that a structure might be attained which would be indistinguishable from a structure built up originally by the placing of atoms in the corresponding uniform pattern in space. The finely twinned phase may thus be regarded as a transition phase between two (real or possible) homogeneous crystalline phases of different structure, just as a mechanically finely divided crystalline phase may be considered as a transition between the crystalline and amorphous phases.

The finely twinned and finely powdered conditions may thus both be treated as unstable variants of corresponding homogeneous phases, some of whose properties have been changed in accordance with the amount of work done in bringing about the subdivision or twinning.

Mügge's etching experiments on crystals have indicated that the atoms at a boundary between twinned portions act as if they were on a free surface.

This view is supported by the experiments of Endell & Rieke[1] on the conversion of quartz into cristobalite. Fine powdering of a homogeneous crystal greatly accelerates its rate of conversion, but twinned structure accelerates it still more. In other words, the individual units of the twinned crystal invert as if they were free fragments of quartz.

Subdivision due to change of temperature

Internal rearrangements due to change of temperature are a frequent cause of fine subdivision in silica. Five effects must be distinguished.

The first may be considered purely mechanical. It is the effect of *non-uniform temperature* through a homogeneous fragment. If the temperature is different in different parts of the fragment, strains will be set up because of the different thermal dilatation of those parts, and the strain may become so large that fracturing results. This is particularly true at temperatures near a high-low inversion-point. Such an inversion is usually accompanied by an appreciable change of volume, and if one part of the crystal fragment inverts before another part, the two parts are almost certain to be torn asunder.

The second effect is also mechanical, or perhaps it would be better

[1] Endell & Rieke, article cited in V, note [28].

called "geometrical," but the result is not fracturing but *twinning*. It will be described in Chapter XII in the discussion of the symmetry of high-quartz and the twinning accompanying the inversion. Briefly restated: the twofold axes of low-quartz are polar, those of high-quartz are not, hence if the inversion from high to low starts at two points in the crystal it is an even chance that they will be oppositely directed, giving a Dauphiné or orientational twin.

The third effect may be regarded as partly mechanical, and partly thermal. Like the first, it arises from non-uniform temperature and its resulting strain, and like the second, it results in twinning instead of fracturing. It is analogous to the twinning produced by a stress, except that the temperature does play an important part by increasing the mobility of the atoms and atom-groups so that twinning is readily brought about, although it would have been impossible to produce it at a lower temperature by differential pressure alone.

The fourth effect may be considered as mainly thermal. It does not depend upon non-uniformity of temperature and upon high-low inversions, but results from the sluggish inversions. The temperature in the fragment may be quite uniform, but if it is above or below the range of stability of the existing form there will be a constant movement of the atoms toward the more stable rearrangement. As the stable arrangement becomes perfected in various parts of the crystal these parts will tend to separate from the parts not yet converted and subdivision of the fragment will result.

The fifth effect is seen in the breaking up of cristobalite at its high-low inversion-point. There is no geometrical or crystallographic reason, so far as I am aware, why a large homogeneous unit of high-cristobalite should not invert to a large homogeneous unit of low-cristobalite, as usually happens with the similar inversion in quartz. The actual result, however, is always the production of a very finely divided product. A hypothetical explanation is offered in Chapter XVI.

Subdivision of quartz by change of temperature

The first three effects described above cover the mechanical break-up and alteration of structure by twinning which is usually observed when quartz is heated or cooled rapidly through the inversion-point at 573°. These effects are discussed more fully elsewhere (see XII and XX). Some notes may be added here on the fourth or thermal effect.

The conversion of quartz into tridymite or cristobalite by heating at temperatures above 870° seems always to be preceded or accompanied by a breaking up of the quartz into very small fragments. The facility with which this break-up occurs differs greatly in different specimens of quartz.

Crystallographically homogeneous clear unstrained crystals of quartz show relatively few cracks even after prolonged heating, and even these

may be due partly to unequal temperature distribution during heating or cooling. Optically anomalous quartz crystals (see VIII) break into very fine fragments. Holmquist [2] estimated that 10,000 to 20,000 such fragments were formed out of a piece about 0.6 mm in diameter during the burning of a silica brick. The diameter of the fragments was thus of the order of magnitude of 0.02 mm.

White vein quartz is converted into a chalky mass of cristobalite, containing a few residual quartz fragments, in the same manner as optically anomalous homogeneous quartz, breaking up first into numberless fine fragments.[3]

Subdivision of cristobalite

The fine subdivision of cristobalite when it passes from the high- to the low-modification has already been mentioned. The subdivision is sometimes so extreme that the product appears to be isotropic. It belongs then in the "micro-aphanitic" class of micro-forms (see X).

The micro-aphanitic products obtained by calcining chalcedony and flint at 1430 to 1460° have the same fundamental atomic arrangement as well-crystallized cristobalite. This is proved by the nearly complete identity of pattern in Hull's X-ray powder photographs of the three.[4] Of the two products, that from flint lies the nearer to cristobalite in density and refractive index.

Effect of fine subdivision and twinning on the temperatures of the sluggish inversions and the melting-points

There is no evidence to show that the inversion-temperatures of quartz to tridymite and tridymite to cristobalite, or the metastable point quartz to cristobalite, are changed by fine subdivision by as much as 10°. These points are difficult to determine in the first place, and are not known with certainty closer than ± 10°. Practically all available data are in agreement with the temperatures given in IV. Therefore it is hardly to be expected that effects of fine subdivision can be proved without new and detailed investigations of the sluggish inversions, investigations more precise than any that have yet been made.

The effect of fine subdivision on the melting temperature of cristobalite may possibly be great enough to account for some of the minor discrepancies among various observers, say 10 to 15°, but is certainly not as much as 50°. Powdered cristobalite made at 1450° from vitreous silica, from pegmatite quartz, and from chalcedony—the latter two being of subnormal density and presumably very finely subdivided, with submicroscopic pores—remains quite loose in texture after 2 hours' heating at 1600° as well

[2] Article cited in V, note [9].
[3] Holmquist, article cited.
[4] Washburn & Navias, article cited in V, note [68].

as after 10 minutes at 1650°, showing that no appreciable melting has occurred at these temperatures.[5]

Effects of fine subdivision and twinning on rates of transformation

While the effects of fine subdivision and twinning upon equilibrium temperatures have not yet been shown to be considerable, the case is very different with the *rates* of inversion.

The large effects of fine subdivision and of twinning upon the rate of transformation of quartz into cristobalite are evident from the data in Table IX.1 (from Endell & Rieke[6]) and the curves of Figure IX.1.

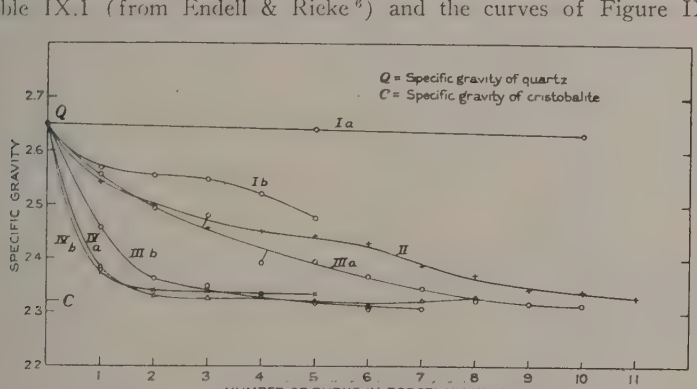


Fig. IX.1.—Diagram showing the decrease of density caused by heating different varieties of quartz, indicating qualitatively their rates of transformation into cristobalite. Each burn was made in a porcelain kiln, the temperature being above 1300° for 12 hours, including 6 hours above 1400°, maximum, 1450°. The numbers on the curves refer to Table IX.1.

The table and figure represent the effects of repeated burnings in a porcelain kiln upon the density of the materials studied. The decrease of density from that of quartz, 2.65, toward that of cristobalite, 2.33, is a qualitative, and roughly quantitative, measure of the relative amount of cristobalite produced at each successive heating.

Curves Ia and Ib presumably show the effect of fine mechanical subdivision alone, since it is unlikely that the fine grinding of the homogeneous crystal produced any other effect than merely to subdivide it. The accelerating effect of this subdivision is seen to be relatively large.

The finely twinned pegmatite quartz (Curves IV) is not converted into cristobalite quite as rapidly as is indicated by the decrease in density. Micro-

[5] Rieke & Endell, article cited in V, note [14].

[6] Rieke & Endell, p. 52 of article just cited; also partly in Endell & Rieke, p. 47 of article cited in V, note [18].

TABLE IX.1.

EFFECT OF REPEATED BURNINGS IN A PORCELAIN KILN UPON THE APPARENT DENSITY OF SPECIMENS OF QUARTZ (ENDELL & RIEKE).

No. of curve in figure	Kind of quartz	Condition of quartz	Original sp. grav.	Sp. gravity after burning in porcelain kiln n times										
				n=1	2	3	4	5	6	7	8	9	10	11
Ia	Homogeneous quartz crystal from St. Gotthard	Fragments	2.65					2.64					2.63	
Ib	do	Fine powder	....	2.568	2.553	2.547	2.519	2.475						
II	Quartz sand from Hohenbocka	Sand	2.651	2.591	2.502	2.456	2.450	2.442	2.428	2.386	2.369	2.343	2.338	2.328
IIIa	Pseudomorphous vein quartz from Taunus, strongly twinned	Fragments	2.651	2.555	2.492	2.478	2.391	2.394	2.366	2.344	2.321	2.316	2.313	
IIIb	do	Fine powder	....	2.456	2.361	2.349	2.333	2.317	2.306	2.307				
IVa	Twinned quartz from pegmatite dikes in Saetersdalen, Norway	Fragments	2.65	2.383	2.33	2.325	2.331	2.32	2.31	2.322	2.327			
IVb	do	Fine powder	....	2.374	2.34	2.34	2.335	2.333						

scopic examination shows unchanged quartz even after several heatings but the cristobalite formed is of low apparent density (2.28, as shown by complete conversion of the material in 2 hours at 1600°) because of cracks and pores, and the mixture of quartz and cristobalite would therefore arrive at the average density 2.33, characteristic of cristobalite, when 15 per cent or more of the quartz still remained untransformed.

The same appears to be true of the twinned vein quartz (Curves II). In this case the conversion is probably aided by the thermal breaking-up of the larger grains, a phenomenon which appears to be connected with a pseudo-biaxial character in the crystals (see also VIII).

Similar effects of subdivision and twinning similar to those illustrated in Figure IX.1 appear also at lower temperatures, as shown by tests made by Rieke & Endell.[7] Quartz sand (Hohenbocka) heated in a kiln to cones 9 to 10 (about 1300°C) decreased in specific gravity from 2.651 to 2.644, and, on a second burning, to 2.633. This total change, amounting to less than 1 per cent, may be only partly due to the formation of cristobalite, the rest being due to the thermal cracking of the quartz grains. Heating to cones 7 to 8 (about 1250°) has hardly any measurable effect upon the specific gravity of this sand.

Powdered Norwegian vein quartz, on the other hand, decreased in specific gravity, after one burning to cones 7 to 8 (1250°), to 2.56, a change of 2.9 per cent.

The accelerating effect of twinning upon the rate of conversion of quartz to cristobalite has been further shown by experiments by Endell & Rieke on a number of specimens of twinned vein-quartz, and banded-quartz from Zillertal, Tirol, Austria. Single heatings to 1450° in a porcelain kiln caused large decreases in density. Detailed results have not been published.

The same observers[8] noticed that finely twinned pegmatite quartz was converted by heating at 1450° into two kinds of material, as shown by microscopic examination. There were present weakly birefringent particles of about the same index as cristobalite, together with large masses of material so permeated with the finest of cracks and pores as to appear almost isotropic. The amount of the sudden expansion at about 230° when this material is heated indicates that both of the materials described are cristobalite.

Houldsworth & Cobb[9] tested the effect of fineness on the rate of transformation of Welsh quartzite (98.78 per cent silica) at 1170°. The amount of transformation was judged from the form of the dilatation curve of the powder bonded with 3 per cent of $CaSO_4$ into a bar. Material ground to pass a 20-mesh I.M.M. sieve showed, after burning, a distinct cristobalite inversion, but a much larger quartz inversion. Material ground to a fine flour, on the other hand, showed nearly twice the amount of cristobalite expansion, while the quartz expansion had become subordinate.

Historical notes

The sharp contrasts in the rates of inversion of different kinds of quartz into cristobalite, described in preceding pages, also appear in the early experi-

[7] Rieke & Endell, article cited in V.
[8] Endell & Rieke, article cited in V, note [10].
[9] Article cited in V, note [20].

ments of H. Rose[10] (1859). He found that a large clear crystal of quartz, heated 18 hours in a porcelain kiln, remained unchanged in appearance and in density (2.650), while the less transparent and somewhat fractured quartz, forming the base or matrix of the same crystal, after the same treatment fell to a white powder of average density 2.613. A similar crystal, finely powdered, decreased in density to 2.394 on the first heating, and to 2.329 on the second.

G. Rose[11] in 1869 continued and amplified these experiments, finding that clear crystals of quartz from Marmarosch, from Jerischau in Silesia, and from Switzerland, all remained little affected by heating; while an equally clear crystal growing on chalcedony in amygdaloidal rocks from Iceland, a fragment of amethyst from Brazil, and an amethyst growing on columnar quartz at Wiesenbad near Annaberg (Silesia), all fell to a white powder after similar heating. The significant difference between these two groups was perceived by Rose, namely, that the latter three were twinned quartz, which transforms much faster than untwinned. Having observed that the inversion begins at the surface of fragments and penetrates along cracks, he suggested that the more rapid conversion of the twinned quartz was caused by its cracking to pieces more easily when heated.

Effect of fine subdivision on vaporization. Sintering

One important effect of very fine subdivision of a substance is to increase its vapor pressure. If larger grains or drops are present, they will therefore tend to grow at the expense of small grains or drops, since the escaping-pressure of molecules from the smaller grains is greater than their escaping-pressure from the larger.

One effect of this distillation process is to bind together the larger grains upon which the vaporized material deposits, by the filling or bridging of interspaces. A loose powder may thereby be converted into a coherent porous cake, or even into a fairly dense and nearly continuous solid. This is one of the two important causes for the phenomenon known as *sintering,* the other being fusion of very small grains on sharp edges and corners while the liquid fills interspaces and recrystallizes there.

There is evidence that differential vaporization of the smaller grains takes place in silica at high temperatures. Thus Endell & Rieke[12] found that although a certain specimen of chalcedony was completely converted into cristobalite by a single heating in a porcelain kiln (maximum 1450°C), yet successive additional heatings of the product under the same conditions caused a steady increase in the apparent density, a change which is in the direction of the true density of cristobalite. (See Table IX.2.) This would indicate a filling of the very small pores which are inaccessible to the liquid used for measuring specific gravity.

Rieke & Endell[13] have also observed that the size of cristobalite crystals

[10] Article cited in IV, note [12].
[11] Article cited in IV, note [20].
[12] p. 247 of article cited in V, note [18].
[13] Article cited in VI, note [27].

made from vitreous silica at 1600° is appreciably greater than the size of those formed at lower temperatures. This may be due to vaporization of the smaller particles at 1600° and redeposition of the silica on the larger crystals.

Although there is evidence, as above described, of differential vaporization in cristobalite, it is apparently not active enough to cause much sintering. Powdered cristobalite made at 1450° from pegmatite quartz, chalcedony, and vitreous silica remains quite loose after 2 hours' heating at 1600° as well as after 10 minutes at 1650°.[13]

Podszus[14] found that a high-temperature mercury-vapor arc inside of a thin-walled narrow tube made of powdered silica brought about sintering.

TABLE IX.2.

EFFECT OF SUCCESSIVE HEATINGS IN A PORCELAIN KILN (1450°) UPON THE APPARENT DENSITY OF CRISTOBALITE (BY PYKNOMETER).

Original form of silica	Chalcedony from Minas Geraes, Brazil
Original specific gravity	2.60
Specific gravity after 1 heating	2.16
" " " 2 "	2.17
" " " 3 "	2.17
" " " 4 "	2.19
" " of cristobalite	2.33

The tube became gas-tight and reached a limiting shrinkage. The original porous opaque tube (of 2 mm bore and 0.2 to 0.5 mm wall) became dense, with milky translucence. The temperature of the silica experiment is not stated, but alumina was sintered at about 1700°, although its melting-point is 2050°.

According to the opinion of Podszus, the effect depends upon the electrical conditions as well as upon the temperature, since similar material subjected to high temperature only, in a vacuum or neutral atmosphere, did not sinter appreciably. He suggests as an explanation for his results that the inner and outer walls were differently charged electrically, to such a degree that the surface tension of the grains was reduced to a much greater extent on one wall than on the other. The oxide thus tended to move in one direction, in this case toward the inner wall, redepositing there and building up a dense shell. I know of no further evidence in support of this hypothesis.

[13] Article cited in VI, note [37].

[14] PODSZUS, E., *Zur Frage der Sinterung und Frittung,* Archiv. Phys. Chem. Glases u. keram. Massen (Sprechsaal) (1912) 1: No. 1, p. 2.

Chapter X. THE MICRO-FORMS

General classification

In Chapters IV, V, and VI we have discussed the mutual relations among eight well-defined solid modifications or phases of silica. In the preceding chapter we have seen that fine subdivision and twinning of the phases may modify their properties, and later pages will show that the properties may be so much affected that the phase which forms the basis of the aggregate can not readily be identified. This fact leaves indeterminate a number of kinds of silica whose relationships to one another are not so clearly defined as are the relationships among the eight better-known phases. We might call them "indeterminate varieties of silica" until we learn more about them, but since their obscurity is due almost entirely to their fine grain the term "micro-phases" or *micro-forms* will serve better.

These varieties or micro-forms may be grouped as follows:

A. *Micro-crystalline.* The substance shows definite optical or other evidence of orderly arrangement of its atoms or molecules in space.

B. *Micro-amorphous.* The substance has properties which prove definitely that it is not to be classed with crystalline substances.

C. *Micro-aphanitic.* It is impossible to tell under the microscope whether the substance is crystalline or not. This third classification-group is simply a convenient dumping-place for varieties which have not been sufficiently investigated, by methods other than optical, to place them either in group A or in group B.

Each of these three groups may be further subdivided, for convenience of description, on the following basis:

There are, geometrically speaking, three possible ways of subdividing a homogeneous phase into discrete units of micro-dimensions, namely:

a. Subdivision into parts having *three* very small dimensions. Examples: suspensoid colloid particles, submicroscopic grains.
b. Subdivision into parts having *two* dimensions which are very small, while the third is relatively large. Example: submicroscopic fibers.
c. Subdivision into parts having *one* dimension very small, while the other two dimensions are relatively large. Examples: plates of submicroscopic thickness, adsorbed films.

The micro-crystalline, micro-amorphous, and micro-aphanitic groups may therefore each be subdivided into

(a) *Micro-granular*
(b) *Micro-fibrous*
(c) *Micro-platy*

We now have 9 formal classes, namely:

Aa. Micro-crystalline-granular
Ab. Micro-crystalline-fibrous
Ac. Micro-crystalline-platy
Ba. Micro-amorphous-granular
Bb. Micro-amorphous-fibrous
Bc. Micro-amorphous-platy
Ca. Micro-aphanitic-granular
Cb. Micro-aphanitic-fibrous
Cc. Micro-aphanitic-platy

The micro-fibrous varieties are by far the most abundant micro-forms of silica. Micro-granular varieties are not uncommon. No micro-platy crystalline varieties of silica are known, but micro-platy amorphous or hydrated varieties may possibly exist, particularly in plastic clays.

Micro-crystalline-granular silica

Several modes of formation of micro-granular silica have been discussed in Chapter IX, together with the effects of the fine subdivision on the equilibrium-relations of the substance. The principles mentioned there are applicable to any micro-form whose constitution (whether quartz, tridymite, cristobalite, or vitreous) is definitely known.

I do not know of any micro-crystalline-granular variety whose constitution or properties are obscure, and it is only with such varieties that this chapter is concerned. Mention should be made here, however, of the micro-granular quartz described by Winchell,[1] because of its possible relationship to the micro-fibrous varieties to be described farther on. It occurs as a microscopically isotropic ground-mass containing crystals of recognizable quartz in all gradations of size from mere points of light in the field up to veinlets and patches of crystals. It contains about 98 per cent SiO_2 with 0.5 per cent H_2O and a little iron oxide. The index of refraction is 1.54 ± 0.01. X-ray powder photographs (see XIII) show only the spectrum of quartz, with sharp and intense lines.

Some of the so-called "opal" of cherty rocks, identified as such because of its isotropic character without measurement of its index, may be this same micro-granular quartz.

Micro-crystalline-fibrous silica

Nearly all of the naturally occurring micro-forms of silica are fibrous in structure. These natural micro-fibrous forms, furthermore, are all closely related to the mineral chalcedony. Hence I shall use the term *chalcedonic silica* as synonymous with "natural micro-fibrous silica."

Most specimens of chalcedonic silica can be definitely shown to be mainly, if not entirely, crystalline, but it is still open to question whether

[1] Winchell, A. N., *Isotropic quartz*, Amer. Mineralogist (1924) **9**: 235-237.

or not the crystalline fibers are accompanied by a variable amount of micro-fibrous amorphous silica, or even micro-fibrous hydrated amorphous (opaline) silica.

The purest varieties of chalcedonic silica are generally called *chalcedony,* but this name is not strictly exclusive, for its meaning ranges rather indefinitely away from practically pure silica, in micro-crystalline form, into varieties containing various other substances as admixtures, and particularly into varieties containing water. For the present we are concerned only with those which consist of practically pure silica.

The color of chalcedonic silica is nearly always due to impurities, and the external form of the aggregate of fibers depends upon conditions of deposition. Hence these two characters, color and visible structure, though widely used in other classifications and still the basis for a great variety of common names, are not of much use in a scientific classification.

The properties of chalcedonic silica fall nearer to those of quartz than to those of any other of the principal forms. This will be seen in later chapters, where the particular properties are considered. There is enough difference, however, to justify the statement that chalcedony is not quartz, nor even a "variety of quartz," if we mean by "variety" a modification whose properties could have been foretold completely from the properties of the parent substance.

Classification of micro-crystalline-fibrous silica

A scientific classification of micro-fibrous-crystalline silica into subclasses of definite properties is not now possible because of lack of data. The first logical possibility that suggests itself is that quartz, tridymite, and cristobalite might each develop under certain conditions in a fibrous habit of growth, giving us three micro-fibrous-crystalline forms. Added to these possibilities is the more remote one that other silica structures, not yet discovered in the form of visible crystals, might exist in micro-fibrous form.

At present we know only that several specimens of chalcedonic silica consist, at least in part, of silica having the structure of low-quartz. This has been shown by X-ray evidence. But the specimens studied have been taken at random, and their other properties are not known. Certain other specimens have exhibited high-low inversion phenomena similar to those of quartz, though not identical therewith in all respects.

On the other hand, specimens have been found whose properties suggest that they are micro-fibrous tridymite. This interpretation has not been satisfactorily confirmed.

What is needed now is a correlation of various physical properties with X-ray evidence of structure on selected natural specimens. Better still would be experiments to produce micro-fibrous silica under known conditions, with accompanying correlation of structure and properties.

Classification by optical properties

Some of the French mineralogists have attempted a classification of chalcedonic silica based upon optical properties.

In the first place it is not difficult to separate the main bulk of the specimens, whose refractive index and density approach those of quartz, from certain rarer specimens of lower index and density, supposed by some investigators to be allied to tridymite.

The first lot, which we may for the moment call *quartzoid chalcedonic silica,* is then classified on the basis of the two secondary optical properties: (a) optical character of the substance, and (b) optical character of the elongation of the fibers (see XXXII). Since there are 4 permutations of these 2 properties, 4 kinds of quartzoid chalcedonic silica are logically possible, 3 of which have been observed. These permutations and the names given to them are listed in Table X.1.

TABLE X.1.

CLASSIFICATION OF MICRO-CRYSTALLINE-FIBROUS SILICA ACCORDING TO OPTICAL CHARACTER AND ELONGATION.

Optical character	Elongation	Name proposed for natural mineral	Name proposed by
+	+	Quartzine	Michel-Lévy and Munier-Chalmas *
+	—	Chalcedonite	Becker †
—	+	(Not known)	....
—	—	Pseudo-calcédonite	Lacroix ‡

* MICHEL-LÉVY & MUNIER-CHALMAS, *Mémoire sur diverses formes affectées par le reseau élémentaire du quartz,* Bull. Soc. Franc. Mineral. (1892) **15**: 159-190, especially p. 166.

† BECKER, G. F., U. S. Geol. Survey, Monograph 13, p. 390 (1888).

‡ LACROIX, A., *Sur une forme de silice optiquement négative,* Compt. rend. Acad. Paris (1900) **130**: 430-432.

Some specimens of the negatively-elongated type of fibrous silica known as chalcedonite have a twisted or helical structure which is revealed by their birefringence. The birefringence varies continuously along the fiber through successive maxima and minima, an effect which can be explained by assuming a bisectrix which rotates around the axis of the fiber while remaining perpendicular thereto. This character may mark a further sub-variety, called by Lacroix [2] *calcédonite à enroulement,* which may be translated *helicoid chalcedonite.* Like quartz, it may be either right-handed or left-handed.

It occurs to me that this peculiarity may possibly be correlated with the polysynthetic twinned variety known as "twisted quartz" (see XXV). The crystallographic relations would fit this interpretation.

[2] LACROIX, A., Mineralogie France (1901) 3, Pt. 1: p. 125.

Another sub-variety [3] related to the optically positive pair (quartzine and chalcedonite) in Table X.1 is produced by elongation of the fibers at an angle to the *c*-axis, instead of parallel or perpendicular thereto. This development yields the fibrous variety called *lutecine*, whose aggregation into crystal-like hexagonal bipyramids forms the mineral *lutecite*.

We may consider next chalcedonic silica of lower index and density. Only one variety of this class has been named and studied, namely, *lussatite*.[4] It has been assumed to be a micro-fibrous variety of tridymite, but this interpretation is in doubt.

The names of the varieties are brought together in Table X.2.

TABLE X.2.

CLASSIFICATION OF CHALCEDONIC SILICA ON THE BASIS OF OPTICAL PROPERTIES.

Quartzoid chalcedonic silica:
- Positive:
  - Quartzine (Positive elongation)
  - Lutecine (Elongation at an angle)
  - Chalcedonite (Negative elongation)
    - Helicoid chalcedonite
- Negative:
  - Pseudo-chalcedonite

Tridymitoid chalcedonic silica:
- Lussatite

None of these micro-fibrous varieties has been made and studied experimentally. Until they shall have been so studied, and until their properties shall have been definitely related one to another as well as to their mode of origin, it will hardly be worth while to attempt further division or classification on the basis of properties which may or may not be of fundamental significance. Strong doubts that these optical properties have any such significance has been raised by the studies of Wallerant,[5] Hein,[6] Leitmeier,[7] and others.

On the other hand, there is no reasonable doubt that optical differences do exist and that they are recognizable under the microscope. They furnish, therefore, a possible basis for further study.

The discovery by Cornu and Leitmeier [8] of a variety of chalcedonic silica which consists of an intimate intergrowth of optically positive and optically negative fibers is discouraging to any hope of correlating the above-mentioned optical characters with the conditions of formation, although it does not mean that such a correlation is impossible.

[3] MICHEL-LÉVY & MUNIER-CHALMAS, p. 174 of article cited in Table X.1.

[4] MALLARD, E., *Sur la lussatite, nouvelle variété minérale cristallisée de silice*, Bull. Soc. Franc. Min. (1890) **13**: 63-66.

[5] WALLERANT, F., *Mémoire sur la quartzine . . .*, Bull. Soc. Franc. Mineral. (1897) **20**: 52-100, pls. 1-4.

[6] HEIN, H., *Untersuchung über faserige Kieselsäuren und deren Verhältnis zu Opal und Quarz*, Neues Jahrb. Min. (1908) Beil.-Bd. **25**: 182-231, pls. 6-7.

[7] LEITMEIER, H., *Beiträge zur Kenntnis des Verhältnisses zwischen Quarz, Chalcedon und Opal*, Centralbl. Mineral. **1908**: 632-638.

[8] DOELTER, Handbuch der Mineralchemie (1914) II, **1**: 165.

The classification and naming of the many natural varieties of micro-fibrous silica will be considered again in the chapter on the silica minerals (XLII). For the present it need only be said that when the commoner terms are used in this book they have approximately the meanings indicated below:

Chalcedony = waxy, translucent, natural, micro-crystalline-fibrous silica.
Flint = cloudy, dark gray or brown or black, opaque, natural, micro-crystalline silica.
Chert = any opaque natural micro-crystalline or micro-aphanitic silica whose structure or environment do not permit it to be otherwise classified.

Experimental data on the constitution of the micro-forms

Recognition of the micro-forms

The recognition of crystallinity under the microscope depends primarily on recognition of *birefringence* (see Chapter XXXII), and this remains true in aggregated materials such as those we are now dealing with. In most cases, especially of inorganic substances, the statement that a substance seen under the microscope is birefringent is equivalent to saying that it is crystalline and that its crystal symmetry is not isometric. On the other hand, a state of strain in a homogeneous glass or in an isometric crystal produces a weak birefringence; hence the mere existence of this quality cannot be taken as sufficient proof of non-isometric crystallinity.

Limits to the study of the size and shape of very small fragments are set by the *resolving power* of the microscope. The resolving power for small grains (and for fine fibers such as those of chalcedony) is limited primarily by the wave-length of the light used. As this is of the order of 0.5 μ, it should be possible to see a colorless object of a diameter as small as 0.3 μ, if it lies alone in a colorless medium of very different refractive index.

The limit of size below which fibrous structure and crystallinity are no longer evident optically therefore varies greatly with the character of the material. The amount of interstitial material between the fibers, the difference of refractive index between interstitial material and fibers, the thickness of the section examined, and various other factors, all affect the decision.

If the birefringence is very strong it can be detected in grains or fibers which are near the limiting size resolvable by the microscope. The forms of silica are so weakly birefringent that if a silica fiber is less than about 3 μ in diameter its birefringence is not definitely observable. But if fibers smaller than 3 μ, even very much smaller, are closely aggregated, and are oriented so that their optical effects are added together, the birefringence may be pronounced.

If such fine fibers or grains are oriented at random no definite birefringence will be observed, and only a slight lighting of the field between crossed nicols will be seen. Aggregates whose fibers have orientation intermediate between the random distribution and perfectly additive parallelism may show a variety of effects when a thin section is rotated under the microscope in polarized light, such as mosaic and spherulitic structure, wavy extinction, and fibrous extinction. Although in general such a effect as fibrous extinction is not distinguishable from the effect of strain, yet in a substance like chalcedony it may be taken as evidence of fibrous structure even though the fibers may be so small as to be invisible.

The use of the ultra-microscope, employing ultra-violet light, does not help much, because the birefringence, although larger than in the visible spectrum, is still not very large. A more promising direction to turn might be just the other way, toward the ultra-red (see Fig. XXXII.3). Here, although the resolving power falls off because the wave-length is greater, it gains more than proportionally because the presence of absorption bands in the ultra-red spectra of silica is accompanied by strong birefringence. So far as I know, there is at present no practicable way of studying the ultra-red through a microscope.

When the examination of optical properties completely fails to indicate the existence of fibers the fracture may indicate a fibrous structure. This is true of the hydrated ferric oxides, but is not so useful in examining the forms of silica.

If microscopic examination has failed to show whether the micro-form is crystalline or amorphous, it has to be called "micro-aphanitic" until some other means is found for deciding the question.

A micro-aphanitic variety of silica may consist entirely of submicroscopic crystals, or it may consist entirely of truly amorphous particles, or it may be a mixture of crystalline and amorphous. Le Chatelier has suggested that since the high-low inversions are so characteristic of the three well-known crystalline forms, quartz, tridymite, and cristobalite, the constitution of a micro-aphanitic form may be determinable by observing the change of some property, such as specific volume, through the range of temperatures within which the high-low inversions occur (100 to 600°). This method has been used to a limited extent.

Chemical methods were early suggested as an aid in identifying microcrystalline silica, particularly the rate at which a specimen dissolves in alkaline solutions. But Rammelsberg [9] showed that differences in dissolving-rate in caustic potash afforded no certain criterion for distinguishing crystalline (quartzitic) and opaline silica. A series of experiments on 19 specimens gave all sorts of dissolving-rates and showed that no conclusions can be drawn as to the relative amounts of "quartz" and opal in any given specimen. Leitmeier [10] reports a similar experience.

[9] RAMMELSBERG, C., Ann. Phys. u. Chem. (Poggendorff) (1861) 112: 177-192.
[10] LEITMEIER, H., article cited.

X-ray evidence

The most certain qualitative method of getting at the constitution of a micro-aphanitic variety is to take an X-ray photograph of it. The occurrence in the photograph of definite lines or spots is almost conclusive proof of the existence of an orderly structure, which means, usually, crystallinity. Such a photograph does not prove, however, that the material is *wholly* crystalline.

The opposite case is more definite. The complete absence of any pattern of sharp lines or spots in the photograph is good evidence that the material is truly amorphous, containing very little, if any, crystalline matter.

For a number of years after the discovery of the X-ray patterns produced by crystals it was supposed that every substance has a pattern of its own, not duplicated by any other substance. But instances have been found recently of substances [11] which have different compositions yet give X-ray patterns which are either identical or differ so little that they can be distinguished only by the most careful examination and measurement.

Data on the constitution of the micro-crystalline varieties

Chemists and mineralogists have examined a great many specimens of chalcedonic silica, using one or more of the criteria just reviewed. Judged by these criteria, the varieties of silica usually grouped under the names "chalcedony," "flint," and "chert" are micro-forms of class b (see p. 152), namely, of microscopic or submicroscopic *fibrous* structure. Furthermore, it appears that most of them are wholly or partly *crystalline*.

The next important questions concern the structure of the fibers themselves. Does the subdivision into units of such small dimensions have in itself an effect on the structure? If not, have the fibers the structure of one of the mega-phases,—quartz, tridymite, or cristobalite,—or are they something different from any of these?

In the first place, there is no reason to believe that mechanical subdivision of a crystalline substance down to magnitudes of the order of 1.0 to 0.5 μ has any influence on the interior structure of the particles. X-ray photographs confirm the expectation that the structure remains unchanged in a micro-phase of class a (micro-granular), since photographs of certain suspensoid colloids show the same diffraction patterns as coarsely powdered crystals of the same substance.

The increased energy content, which expresses itself in effects upon inversion temperatures, melting-points, etc., as discussed in Chapter IX, is thus derived almost wholly from the increased surface per unit mass.

[11] Wyckoff, Greig, & Bowen, Amer. J. Sci. (1926) (5) **11**: 459-472. Wyckoff & Morey, Ibid. (1926) (5) **12**: 419-440. Sosman & Posnjak, J. Wash. Acad. Sci. (1925) **15**: 329-342.

There is also no evidence that micro-twinning has any effect on the internal structure of the twinned units.

We may proceed, then, to the second question. To this a definite, though partial, answer can be given for at least two specimens of fibrous micro-forms, namely, the black French flint and the chalcedony from Yellowstone Park investigated by Washburn & Navias.[12] X-ray photographs of these two, made by A. W. Hull by the powder method, show the same pattern of lines as crystalline quartz. It is highly probable, then, that a considerable proportion of the fibers of these two specimens possesses internally the atomic arrangement characteristic of quartz.

As to the presence of amorphous fibers in these same specimens no such definite statement can be made. Amorphous silica has a characteristic band in the X-ray powder spectrum, but no such band is visible in Hull's photographs. At the same time, his photograph of vitreous silica, which should have contained the band, is also quite blank, showing that the conditions of exposure and development were not such as to bring it out strongly. Hence its absence from the chalcedony and flint photographs does not prove the absence of a considerable proportion of amorphous silica.

The evidence of the high-low inversions will be discussed at a later page.

Lussatite

Mallard's original lussatite [13] was described by him as a distinct new modification of silica. Lacroix [14] suggested its classification as a micro-fibrous form of tridymite, the other micro-crystalline varieties being allied to quartz. Slavik [15] studied additional specimens and concluded from optical properties that lussatite has the structure of tridymite.

Its natural associations, on the other hand, are not those usually expected for tridymite, for it is always accompanied by opal, true chalcedony, or quartz. Rosenbusch [16] and Hein [17] may be right in assuming that lussatite is only quartzine intimately mixed with opal. An X-ray powder photograph of the type material would settle very quickly the question whether the underlying structure is that of quartz or tridymite.

Mallard.[18] has also noted the occurrence, in charcoal pig-iron, of fine white fibers which could be separated mechanically, and which were birefringent, with parallel extinction, positive elongation, and density of about 2.30. They dissolved easily in an alkaline solution. He considered this material to be tridymite elongated in the direction of the positive bisectrix. No further study of it has been made.

[12] Article cited in V, note [68].
[13] Mallard, E., article cited in note [4].
[14] Lacroix, A., *Minéralogie France* (1901) 3: p. 168.
[15] Slavik, F., Centralbl. Mineral. **1901**: 690-692.
[16] Rosenbusch, H., Mikroskop. Physiographie (1905) 1, Pt. 2: p. 390.
[17] Hein, H., p. 228 of article cited.
[18] Mallard, E., p. 172 of article cited in IV, note [18].

Historical notes on the micro-crystalline varieties

H. Rose[19] (1859) distinguished between "crystallized" (krystallisirte) silica, which included rock crystal, quartz, amethyst, and sandstone; and "crystalline" (krystallinische) silica, which he usually referred to by the words "dichte (krystallinische)" and which included chalcedony, chrysoprase, hornstone, flint, and some petrified woods and similar deposits. The slightly lower density of the second group was recognized, as well as its more rapid dissolving-rate in alkalies or HF.

This distinction between crystallized and crystalline has now been quite forgotten, since our methods for recognizing crystallinity have been so much improved. The distinction between Rose's two groups is now usually made by means of the words "crystalline" and "micro-crystalline."

The principles governing the interference phenomena seen in fibrous minerals under the microscope were clearly stated by Babinet in 1837. He showed that an aggregate of fibers of irregular size can be distinguished from an aggregate in which the fibers are nearly all of the same diameter, as in fibrous quartz, and showed also how the diameter of the fibers can be determined. The detailed application of the principles to micro-fibrous silica did not follow until many years later.

Micro-amorphous varieties of silica

Micro-amorphous-granular silica

Silica in a finely divided form, in grains so small that the microscope can not always be depended upon to reveal whether or not they are crystalline, can be obtained by two general methods: (1) precipitation from solution, and (2) deposition from a vapor.

Precipitated silica can be prepared in the following ways:

(a) By the addition of an acid to a solution such as water-glass. The precipitate of hydrated SiO_2 is washed, dried, and heated hot enough to drive off all the water.

(b) By passing the vapor of SiF_4 into water. The precipitate of hydrated SiO_2 is filtered off and heated to drive off all water.

These different kinds of precipitated silica are amorphous, that is, their atoms are not arranged in an orderly pattern. In a general way, their properties are similar to the properties of vitreous silica (silica glass) which has been ground very fine.

The experimental data

The amorphous character of precipitated silica is demonstrated with certainty by its X-ray pattern. Kyropoulos[20] made powder photographs (see

[19] Rose, H., article cited in IV, note [12].

[20] Kyropoulos, S., *Zur Unterscheidung der Aggregatzustände verschiedener SiO_2-Arten mittelst ihrer Röntgenstrahlen-Interferenzbilder,* Zeitschr. anorg. allg. Chem. (1917) **99**: 197-200, pl. 9. [The original plate in the Zeitschrift was wrongly labeled and has been subsequently replaced.]

XIII) of precipitated silica which had been lightly ignited, leaving 3.3 per cent H_2O still present. X-rays from a platinum target yielded only the general blackening resulting from heterogeneous scattering. A similar result was obtained with Kahlbaum's "Alkalifreies Kieselsäurehydrate" (alkali-free hydrated silicic acid). The author's published photographs, however, show the broad band characteristic of amorphous silica (see p. 160) although he himself did not call attention to it.

Küstner & Remy [21] made X-ray powder photographs of precipitated silica, using a tube with copper anticathode. Silica precipitated from sodium silicate with hydrochloric acid and dried 5 hours at 100° gave only a slight general blackening near the center of the photograph (60 kilovolts, 360 milliampere-minutes). The same result was obtained with silica precipitated as above, but heated for 4 hours in a platinum crucible over a blast lamp. The exposures were probably too short to bring out the diffuse band characteristic of amorphous silica.

Braesco [22] has shown that precipitated silica obtained by adding hydrochloric acid to a sodium silicate solution, and dried by preliminary heating to 600°, has the same thermal expansion coefficient as vitreous silica up to 440°, and is, therefore, amorphous. It remains amorphous even when ignited to near 1000°.

The silica obtained by the action of water on SiF_4, followed by drying and ignition up to 900°, is also amorphous, as shown by its thermal expansion coefficient.

Micro-amorphous-fibrous silica

Amorphous silica in micro-fibrous form has been produced under a variety of circumstances, but a relatively high temperature seems to be the condition common to them all. Micro-fibrous amorphous forms have been obtained from electric furnaces, from iron blast-furnaces, from the vicinity of blast lamps operating on silica, and through indirect volatilization of silica. The origin of the fibrous structure is not understood although it is evidently not the result of the simple mechanical stretching of viscous threads.

The experimental data

The most complete data concerning any particular specimen are the data relating to a micro-fibrous silica sent to me in 1914 by Mr. F. J. Tone of the Carborundum Company at Niagara Falls, and said to have been produced in an electric furnace. Mr. Tone's analysis showed it to contain 99.56 per cent SiO_2. It consisted of a compact, silky-surfaced mass of microscopic parallel fibers, and was thought at first to be a new crystalline variety of silica, since fibrousness in minerals is generally taken as evidence of crystallinity. In many fibrous minerals a continuous series can be traced, from coarse crystalline fibers which are large enough for cross-sectioning, down to fibers

[21] Küstner, H., & Remy, H., *Die Struktur des Siliziums*, Physik. Zeitschr. (1923) **24**: 25-29.

[22] Article cited in IV, note [14].

of submicroscopic diameters. We therefore expected to find this specimen to be a fibrous development of cristobalite or tridymite.

Under the microscope it proves to be nearly but not quite isotropic, and to have the index of vitreous silica. Its essentially amorphous character is proved by the absence of any pattern in an X-ray photograph of the usual length of exposure, whether the silica is in the form of powder, or whether the specimen is set up with fibers parallel to the slit of the X-ray box.[23]

Longer exposures of the X-ray film, however, show the interesting feature of a diffuse band similar to that given by vitreous silica and colloidal silica on long exposures.

Under the microscope, furthermore, the material has crystalline properties to the extent that the fibers are faintly birefringent, while their elongation is positive.

We evidently have here a substance which according to ordinary criteria would be called amorphous or glassy, and yet possesses some slight traces of a structure.

It is not impossible that the true index of refraction of the fibers is higher than that of vitreous silica. In the case of such fine structures only the index of the aggregate can be measured, and if fibers of higher index were to absorb water between them the average index of the aggregate would be lowered thereby.

Silica in the form of very fine "cobwebs" is often found in the vicinity of furnaces or blast lamps operating on fused silica. I have collected cottony material of this kind from the top of a carbon-tube electric resistance furnace. I have also received specimens from the quartz-glass department of the Cooper-Hewitt Company of Hoboken, New Jersey.

Some of this latter material evidently consists of fine-spun threads of vitreous silica of normal index of refraction. The rush of gases over or through the soft glass would explain the formation of much of it. In some cases the phenomenon called "electrical spinning" may have had something to do with its production. This phenomenon was described by Boys[24] in 1887 and had been known for many years. When melted rosin, beeswax, shellac, or some similar viscous liquid insulator is placed in an insulated dish connected with a static machine, the material, if it reaches the edge of the dish, is shot out in very fine threads along the electric lines of force. They fly towards a conductor, but if discharged en route, as by the ionized air around a flame, they turn and fly back to the source. Fibrous amorphous silica may conceivably be formed by a similar process, wherever it has an opportunity to become charged, since it is very viscous above its melting point and is an excellent insulator.

Neither mechanical nor electro-mechanical spinning, however, will account for the production of compact parallel or radial bundles of fibers such as the variety described at p. 162 or other varieties to be described in later paragraphs of this chapter.

[23] Unpublished results obtained in 1921 by Dr. E. Posnjak of the Geophysical Laboratory. See also Sosman, R. B., J. Franklin Inst. (1922) **194**: p. 754.

[24] Boys, C. V., *On the production, properties, and some suggested uses of the finest threads,* Proc. Phys. Soc. London (1887) **9**: 8-19; Phil. Mag. (1887) (5) **23**: 489-499.

Wartenberg[25] obtained a radially fibrous deposit of silica by the reduction of SiO_2 and volatilization of silicon in a current of hydrogen. The deposit formed near the end of the cold capillary tube through which the gases were drawn from the furnace and was evidently formed by the reoxidation of Si by H_2O. The fibers were isotropic and of refractive index 1.46.

In experimenting on the sublimation of silica by reduction in a current of hydrogen, Dufour[26] found that when vitreous silica wool was used in a vitreous silica tube, the deposited silica took the form of extremely fine filaments which covered the glass threads, giving them a milk-white instead of a silky appearance, and appearing to emerge from the surface of the glass thread to which they adhered. The filaments were isotropic.

Riddle & Peck[27] found two types of micro-amorphous silica in a Dressler tunnel kiln operated at a temperature in the vicinity of 1450°. Both were evidently deposited from the gases in the kiln. One was "in the form of a white coating, extremely light and fluffy in character, with a smooth outer surface resembling that of a mushroom." This suggests an analogy with the botryoidal forms commonly seen in deposits of the fibro-crystalline minerals chalcedony (SiO_2) and goethite ($Fe_2O_3.H_2O$), although the material is far less dense than these. The composition was 97.32 to 98.42 SiO_2, the remainder being Al_2O_3 and Fe_2O_3. The index[28] was just under 1.46.

The other form was definitely fibrous, the fibers showing a relation to the directions of gas currents.

These deposits result probably from the oxidation of silicon which has either volatilized from the silicon carbide refractories in the kiln, or has been oxidized in place and then volatilized as SiO_2.

Micro-fibrous aphanitic silica

Micro-fibrous varieties of silica have several times been reported as occurring in blast-furnaces for the production of iron. A micro-crystalline variety of this origin, examined by Mallard, has already been described (see p. 160.) The crystalline or amorphous character of the other specimens is not known, and they will have to be classed here as "aphanitic".

H. Rose[29] examined small quantities of a silky fibrous silica, apparently amorphous, obtained from the hearth of an iron-furnace. It consisted of nearly pure SiO_2 with a few inclusions of titanium compounds and graphite. Its density was 2.32, which is about the density of cristobalite.

The fibrous silica classified as "Eisenamianth" was analyzed for the first time by Schnabel[30] in 1852. The specimen examined consisted of short parallel fibers, very soft, of silky luster, and snow white; density, 2.59. It was found in an iron "sow" in the Olsberg furnace in Westfalen, Germany.

[25] Wartenberg, H. v., article cited in VI, note [68].
[26] Dufour, A., article cited in VI, note [69].
[27] Riddle, F. H., & Peck, A. B., J. Amer. Ceram. Soc. (1926) **9**: 1-21.
[28] Peck, A. B., correspondence with the author.
[29] Rose, H., *Ueber die Kieselsäure der Hohöfen,* Ann. Phys. u. Chem (Poggendorff) (1859) **108**: 651-653.
[30] Schnabel, C., *Untersuchung des sogenannten Eisenamianths,* Ann. Phys. u. Chem. (Poggendorff) (1852) **85**: 462.

The composition found was: SiO_2, 98.13; Al_2O_3, 1.24; CaO, 0.46; MgO, trace; FeO, trace; total, 99.83.

Kohlschütter & Tüscher[31] have prepared a micro-aphanitic form of silica by heating pure carborundum in the positive crater of a carbon arc in a current of air, the resulting smoke being then precipitated by a high-tension electrical corona discharge in a separate chamber of the apparatus. A smooth fairly compact deposit of SiO_2 is thus obtained. It has a "feel" like talc; has a faintly bluish color, probably structural, due to a high dispersive power; absorbs considerable amounts of water from damp air and swells slightly; is wet by water without disintegration of the lumps, although it subsequently swells and disintegrates; and is converted into colloidal suspensions, more or less filterable, with the aid of peptizing agents, especially ammonia. A rough comparative "compressibility" of the bulky powder could be determined by shaking it down in a glass tube and then compressing a definite depth with a plunger and weights. The bulk density in grams per cc was determined at the same time. It was found that the more bulky specimens were the more compressible. This relation still held after the powder had been ignited for an hour. The ignition produced only a slight shrinkage which seemed to occur for the most part below 125°.

[31] Kohlschütter, V., & Tüscher, J. L., *Über Darstellung disperser Substanzen in gasförmigen Medien,* Zeitschr. Elektrochem. (1921) **27**: 225-256.

Chapter XI. TRANSFORMATIONS AND INVERSIONS OF THE MICRO-FORMS

The addition of micro-crystalline and micro-amorphous silica to the original list of 5 principal phases: quartz, tridymite, cristobalite, liquid (or glass), and gas, makes it necessary to consider 22 more two-at-a-time permutations in addition to the original 20 (see pp. 60, 86, and 107). Some of the combinations are of little importance, while on others we have considerable information. For the sake of logical completeness all are listed below:

(21)	Micro-crystalline to cristobalite	Changes in micro-crystalline silica at high temperatures
(22)	Micro-crystalline to tridymite	
(23)	Micro-crystalline to quartz	
(24)	Micro-amorphous to cristobalite	Crystallization of micro-amorphous silica
(25)	Micro-amorphous to tridymite	
(26)	Micro-amorphous to quartz	
(27)	Micro-crystalline to liquid (glass)	Fusion and volatilization of micro-crystalline silica
(28)	Micro-crystalline to gas	
(29)	Micro-amorphous to liquid (glass)	Fusion and volatilization of micro-amorphous silica
(30)	Micro-amorphous to gas	
(31)	Gas to micro-crystalline	Production of micro forms by condensation from gas
(32)	Gas to micro-amorphous	
(33)	Quartz to micro-crystalline	Production of micro-crystalline silica from other forms
(34)	Tridymite to micro-crystalline	
(35)	Cristobalite to micro-crystalline	
(36)	Glass to micro-crystalline	
(37)	Micro-amorphous to micro-crystalline	
(38)	Quartz to micro-amorphous	Production of micro-amorphous silica from other forms
(39)	Tridymite to micro-amorphous	
(40)	Cristobalite to micro-amorphous	
(41)	Glass to micro-amorphous	
(42)	Micro-crystalline to micro-amorphous	

Permutations (21), (22), and 23): Changes in micro-crystalline silica at high temperatures

(21) *Micro-crystalline silica to cristobalite*

Micro-fibrous crystalline silica, like quartz and vitreous silica, is transformed into cristobalite by dry heating at 1200° and higher. A characteristic feature of the product is that it has a lower apparent density than cristobalite made from quartz or vitreous silica. This low density is probably due to the finely fibrous character of the original chalcedonic silica and a resulting finely porous character in the cristobalite (see, further, p. 303).

Rate of transformation

The rate of transformation of chalcedonic silica into cristobalite, like that of quartz into cristobalite, is very much influenced by the temperature. In general, it is more rapid than that of quartz.

The rate is almost inappreciable at 900 to 1000°, but becomes easily measurable at about 1200°, and increases with rising temperature.

At temperatures of 1200 to 1400° the rate of transformation of chalcedonic silica is much greater than that of quartz, while at 1500° and higher the difference is not so marked as at lower temperatures.

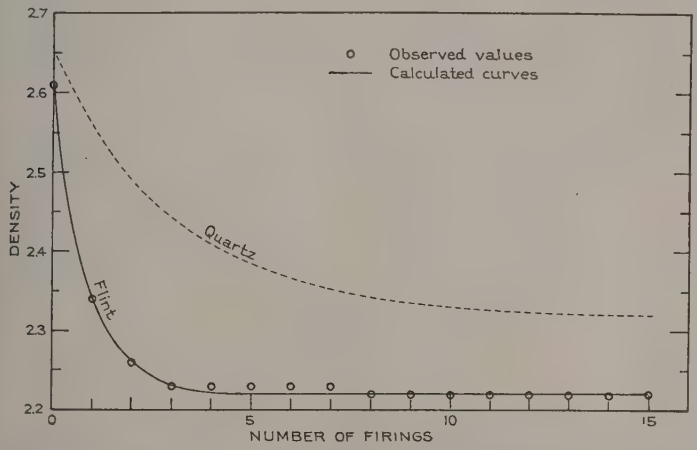


FIG. XI.1.—Effect of repeated firing upon the density of flint, showing its transformation into cristobalite. The curve for quartz is repeated from Figure V.1. (Mellor & Campbell.)

Experimental data on the rate of conversion

Mellor & Campbell[1] have studied the speed of conversion of flint, an impure variety of chalcedonic silica, into cristobalite by making 15 successive burns in a china biscuit kiln to cone 10 (nominally 1330° C), and measuring the density of the product after each burn. The conversion was practically complete after the third burn, so that the opportunity was not so good as with quartz (see p. 67) to test the speed of the inversion by comparison with the formula $x = e^{-KZ}$ in which x is the fraction which remains unchanged at the time Z. Nevertheless, it appears likely that the curve is of the same character as that for quartz, as is shown by Figure XI.1. The calculated curve in this figure is

$$d = \frac{14.87}{6.7 - e^{-1.05N}}$$

in which N is the number of burns. This curve is based on an initial density of 2.61 and a final density of 2.22. For comparison, the curve for quartz is reproduced from Figure V.1.

[1] Article cited in V, note [17].

The contrast in rate between quartz and micro-crystalline silica is shown qualitatively by some burning tests made by Endell[2] on quartzites for silica brick. As in Mellor's tests, the progress of the conversion was followed by means of measurements of density. Endell showed that German cemented-quartzite, containing much chalcedonic cement, underwent large increases of specific volume on its first two heatings in a porcelain kiln (maximum 1450°), but increased very little on three successive heats following the first two. A German quartzite containing a much larger proportion of coarsely crystallized quartz, on the other hand, increased less on the first heating than did the cemented-quartzite, and continued to increase in specific volume with each successive heating.

TABLE XI.1.

EFFECT OF HEATING UPON APPARENT DENSITY OF CHALCEDONY AND FLINT, AS COMPARED WITH QUARTZ. RIEKE & ENDELL.

Kind of quartz	Condition of quartz	Original sp.gr.	Sp. gr. after being heated in kiln to cones 9-10 (about 1300°)	Sp. gr. after being heated in kiln to cones 7-8 (about 1250°)	Sp. gr. after being heated in platinum furnace at 1300° for 2 hr.	Sp. gr. after being heated in platinum furnace at 1200° for 3 hr.	Sp. gr. after being heated in platinum furnace at 1200° for 4 hr.
Quartz sand, Hohenbocka ..	Sand	2.651	2.644 2.633 *	(2.65)			
Pegmatite quartz, Norway	Powder	2.65		2.56			
Chalcedony		2.607	2.40		2.42–2.43		
Flint		2.632	2.26	2.28		2.50	2.48

* Second burning.

The decreasing contrast between the rates for chalcedonic silica and quartz at higher temperatures is shown by the following further comparisons. A quartzite which made poor brick (much coarse-crystaled quartz), another which yielded medium brick, and a third which gave good brick (much chalcedonic cement) all showed about the same amount of conversion, as determined by pyknometer density, after 2 hours at 1500°, although the poor-brick quartzite had been far behind in its degree of conversion in 2 hours at 1250° and 1400°.

Endell[3] also compared 3 American coarse-crystalline quartzites with 2 German cemented-quartzites, again finding that the cemented-quartzites, which contain chalcedonic silica, were the more rapidly converted. A Hessian (German) coarse-crystalline quartzite was similar to the American.

Other similar comparisons are shown in Table XI.1.

[2] Article cited in IV, note [25].

[3] ENDELL, K., *A comparative study of American and German quartzites as raw materials for the silica brick industry,* J. Amer. Ceram. Soc. (1921) 4: 953-960.

The effect of temperature on the rate of conversion of chalcedonic silica is illustrated in the following observations:

Rieke & Endell[4] observed only a very slight decrease in density after 48 hours' heating at 900°, and the change was within the limits of error of the measurement.

Houldsworth & Cobb[5] examined the dilatation curves of flint which had been calcined at 1000° and then ground to flour, and also of this same flour after it had been further fired in a kiln to a maximum of 980° in 48 hours. In neither case was there any indication of the presence of cristobalite in the product before the high-temperature firing began. The results of these and other tests by Houldsworth & Cobb are summarized in Table XI.2. In each expansion test 3 per cent of $CaSO_4$ was added as a binder.

TABLE XI.2.

SUMMARY OF HOULDSWORTH & COBB'S EXPERIMENTS ON TRANSFORMATIONS IN FLINT.

Material	Temperature °C	Time	Expansion test	Index of Refraction	Density
Flint, 20-mesh..	....	....	Rapid expansion 500 to 700°	Over 1.503	2.56
Flint, calcined at 1000° and ground	....	....	Rapid expansion 500 to 600°	....	....
Same	980	48 hours to reach maximum	Rapid expansion 500 to 600°	Over 1.503	2.56
Same	1170	72 hours to reach maximum	Large expansion 200 to 230° Small expansion 550 to 600°	Part over 1.503 Part between 1.481 and 1.503	2.39
Preceding specimen	1390-1410	2 hours	Large expansion 200 to 230°	Mostly between 1.481 and 1.503 Little over 1.503 Little below 1.481	2.33
Preceding specimen	1510-1550	2 hours	Larger expansion 200 to 230°	All between 1.481 and 1.503	2.34

Chalcedony (from Minas Geraes, Brazil) is transformed completely into cristobalite by a single heating in a porcelain kiln (18 hours above 1200°, maximum 1450°). The cristobalite is of characteristically low density, which increases gradually on continued heating (see Table IX.2). At 1600° the transformation is complete after 2 hours.[6]

Flint is transformed into cristobalite by a single heating in a porcelain kiln (maximum 1450°) in the same manner as the pure chalcedony and the

[4] Article cited in V, note [28].

[5] HOULDSWORTH, H. S., & COBB, J. W., *The behaviour of fireclays, bauxites, etc., on heating*, Trans. English Cer. Soc. (1922) **22**: 111-137.

[6] RIEKE & ENDELL, p. 247 of article cited in V, note [28].

product has a characteristically low specific gravity (2.230-2.255) though not as low as that of the cristobalite from pure chalcedony with which it was compared.[6]

Raw "Joynt's silica," a trade variety of the cherty quartz of southern Illinois (from near Tamms) is converted into cristobalite[7] of index 1.478-1.493 by a few hours' heating at 1450°.

Mellor & Campbell[8] found that heating at cone 3 (nominally 1190°C), —time not stated but presumably about 3 hours,—converted 30 per cent of black flint and 35 per cent of gray flint into cristobalite. The difference in rate of conversion between the two kinds of flint was definite, and in fact constituted the only essential difference between them.

Conversion was nearly complete after 3 hours at cone 14 (nominally 1410°C).

Robson[9] heated pulverized "chalcedony" from southwestern Illinois, of which 96 per cent passed a 300-mesh sieve, to a maximum of 1390° in 4½ hours, and found the index of refraction to have been lowered from 1.540 to 1.527. A similar heating to 1410° in 4¼ hours lowered the original index to 1.495.

Corresponding heat treatments of pulverized calcined French flint (85 per cent through 300-mesh) lowered the original index of 1.527 to 1.487 in both cases.

Specimens of the same materials were heated by Rieke[10] to 1430° in a porcelain kiln, and the resulting changes in specific gravity were compared with the effects produced by the same treatment of similar materials used in Germany (see Table XI.3). The data indicate partial conversion of the chalcedony and complete conversion of the flint to cristobalite at 1400° to 1430°.

TABLE XI.3.

EFFECT OF HEATING UPON THE APPARENT DENSITY OF QUARTZ AND CHALCEDONIC SILICA OF VARIOUS TYPES USED COMMERCIALLY IN AMERICA AND GERMANY (RIEKE, 1921).

Material	Source	Used in	Original sp. gr.	Sp. gr. after being heated at 1430°C
Silica sand	United States *	United States	2.67	2.49
Quartz rock	United States *	United States	2.66	2.49
Flint pebbles	France *	United States	2.57	2.28
Chalcedony		United States	2.66	2.32
Vein quartz	Norway	Germany	2.65	2.37
Quartz sand	Hohenbocka	Germany	2.65	2.59
Flint		Germany	2.63	2.23

* Specimens from A. S. Watts, Columbus, Ohio.

[6] RIEKE & ENDELL, p. 247 of article cited in V, note [18].
[7] WASHBURN & NAVIAS, article cited in V, note [68].
[8] Article cited in V, note [17].
[9] ROBSON, J. T., *The influence of heat on the microscopic properties of silica in its different mineral forms*, J. Amer. Ceram. Soc. (1922) 5: 670-674.
[10] RIEKE, R., article cited in V, note [26].

Phenomena of the transformation

Rieke & Endell [11] observed that the product obtained by heating Brazilian chalcedony is not homogeneous, but consists of very small clear particles having small birefringence, together with larger, honeycombed portions whose cellular structure becomes visible only on stronger magnification. Both have a refractive index of 1.48-1.49. Both are probably cristobalite.

Washburn & Navias [12] observed that black French flint after being heated for one minute in a platinum crucible over a blast lamp gave a product having a refractive index between the limits 1.500 and 1.519. Chalcedony (Yellowstone Park) similarly treated came within the limits 1.500 and 1.526. The flint, after being heated 1½ hours at 830°, also came within the limits 1.500 and 1.519, and the index remained the same to the end of a total period of 700 hours at 830°.

Now the indices of quartz are 1.544 and 1.553, of tridymite 1.469 to 1.478, of cristobalite 1.484 to 1.487, and of vitreous silica 1.458 to 1.459. The unknown products mentioned above thus have an index intermediate between quartz and cristobalite. They may possibly represent something new, but it seems more likely that they are submicroscopic mixtures of the initial and final products.

Historical notes

The transformation of flint, by heating in a porcelain kiln, into a chalky, easily powdered substance, which he supposed to be "amorphous" silica, was observed by H. Rose in 1859. One heating of flint of density 2.591 lowered the density to 2.218 in the mass, or 2.237 when finely powdered.

The effect of fine grinding in bringing quartz into the same class with chalcedony and flint, as regards its dissolving-rate in alkalies, etc., was also recognized by H. Rose.

Permutations (24), (25), and (26): Crystallization of micro-amorphous silica

(24) *Micro-amorphous to cristobalite*

Finely divided pure amorphous silica changes into cristobalite at all temperatures between 1000° and 1710°. When heated alone at temperatures below 1000° it remains unchanged, at least for periods of time measured in days or weeks.

The presence of a solution or melt has three effects upon the transformation, as compared with the results when the silica is heated alone: (1) the change is more rapid at a given temperature; (2) the temperature at which the change takes place with measurable rapidity is lower; (3) a larger proportion of tridymite is formed, if the temperature is below 1470°.

[11] Article cited in V, note [18].
[12] Washburn & Navias, article cited in V, note [68].

(25) *Micro-amorphous to tridymite*

The transformation of pure micro-amorphous silica to tridymite has not been observed. Cristobalite is always the first product.

In the presence of a molten solvent or in the presence of water at high temperatures, however, tridymite may be produced from micro-amorphous silica directly, without the intermediate formation of cristobalite. This is known to be true in the stability-range of tridymite, 870 to 1470°, and may possibly occur also in the quartz range, below 870°.

It appears to be a matter of relative rates of solution and crystallization, without much margin in favor of any one of the forms. Unstable and therefore temporary cristobalite may appear at any temperature below 1470°.

(26) *Micro-amorphous to quartz*

The transformation of pure micro-amorphous silica to quartz has not been observed. In the presence of a molten solvent or in the presence of water at high temperatures quartz may be produced from micro-amorphous silica directly, at temperatures below 870°. It never appears above 870°.

The experimental data on the crystallization of micro-amorphous silica

As already remarked in Chapter X, micro-amorphous silica made by the precipitation of water-glass with acids is never quite pure, but holds a few per cent of salts. These impurities have the effect of producing a small proportion of liquid flux if the temperature is sufficiently high.

Pure micro-amorphous silica can be made, however, as for instance by the reaction of silicon fluoride, SiF_4, with water, and the data on the transformations of the pure product will be considered first.

Pure silica

Braesco[13] made pure micro-amorphous silica by the decomposition of SiF_4 with water. It was heated at a temperature below 900°, length of time not stated. The very small thermal dilatation from 15° to 440° showed it to be unchanged amorphous silica.

Houldsworth & Cobb[14] tested the effects of different temperatures and times of heating on pure micro-amorphous silica made by passing SiF_4 into water. The powder was agglomerated into bars with the aid of gelatin, and then heated. The results are given in Table XI.4.

Silica in the presence of salts

When a liquid is present in which the silica is even slightly soluble, the micro-amorphous silica is much less resistant to change than when it is pure

[13] Article cited in IV, note [14].
[14] Article cited in V, note [22].

and dry. This holds true whether the flux is purposely added or whether it results from the presence of a few per cent of adsorbed salts.

TABLE XI.4.

EFFECT OF HEATING UPON MICRO-AMORPHOUS SILICA.

Heat treatment	Expansion test	Examination in index liquids
Bar heated to 700° in muffle..	Same as vitreous silica 15 to 700°	....
Same bar heated at 630° for 72 hours	Same as vitreous silica 15 to 700°	....
Same bar heated at 700° for 26 hours	Same as vitreous silica 15 to 700°	....
Fresh bar heated at 1150-1170° for 4 hours.....	Shows cristobalite inversion	About half cristobalite Little tridymite No quartz
Fresh bar heated at 1430-1450° for 2 hours.....	Shows cristobalite inversion	....

Houldsworth & Cobb[15] prepared micro-amorphous silica by precipitating diluted commercial water-glass with hydrochloric acid, washing, and drying. They found that it held about 5 per cent of Na_2O. The product was heated

TABLE XI.5.

EFFECT OF HEATING UPON IMPURE MICRO-AMORPHOUS SILICA.

Heat treatment	Expansion test
Bar heated 2 hours at 790°.....	Increased rate of expansion at 115-120° Much larger expansion about 200° Small expansion above 300° Contraction 470 to 700°
Same bar heated 70 hours at 650 to 710°	Change at 115° not very noticeable Expansion at 200° larger than before No expansion 500 to 700°
Same bar heated 91½ hours at 680 to 720°	Expansion 200 to 250° greater than before No expansion above 500°
Several successive heatings at about 700°	Expansion about 200° diminishing toward constant value.
Bar after 768 hours' total heating.....	Rapid expansion 150 to 250° Slower expansion 250 to 500° Constant 500 to 700°

for 2 hours at 790° and then subjected to a long series of heatings at temperatures between 650 and 720°, the total time being 768 hours. Microscopic examination showed that it then consisted mostly of particles of index greater

[15] Article just cited.

than 1.481 and less than 1.503, with a small proportion between 1.468 and 1.481, and a few less than 1.468. It was therefore mostly cristobalite with a little tridymite.

The progress of the transformation, however, as shown by expansion tests, is not entirely clear. A summary of the progressive changes is given in Table XI.5.

The evidence of the expansion data would indicate the formation of a small amount of tridymite at the first heating, which was afterwards changed into cristobalite. This is exactly opposite to the normal direction of change at this temperature.

Houldsworth and Cobb also give the following additional data on the conversion of precipitated micro-amorphous silica, containing sodium salts, into cristobalite:

Heat treatment	Expansion test
Heated twice to 700°.....	Slight expansion 15 to 170° Large reversible expansion 170 to 210° Steady expansion 210 to 420° Contraction 420 to 700°
Same bar heated 2 hours at 700°.....	Expansion 170 to 210° about 3 times as large as before

The expansion tests show clearly that a considerable proportion of cristobalite has been produced at 700°.

In contrast to these results of Houldsworth and Cobb below 800° is the experience of Day and Shepherd,[16] who could observe no change in precipitated silica heated for a month at 900°. Braesco also made silica by precipitation from silicate of soda with an acid, and then heated it at 600 to 1000°, time not stated. Its very small thermal dilatation over the range 15° to 440° showed that it was amorphous silica.

The difference in behavior may have been due to greater purity in the case of these last two products.

Above 1000° the precipitated silica always changes initially to cristobalite. Thus Braesco's amorphous precipitated silica, after being heated to 1100°, 1400°, or 1600°, showed the characteristic inversion-expansion of cristobalite between 200 and 300°.

Fenner found precipitated silica to be completely changed to cristobalite after 69 hours at about 1030°.

Kyropoulos[17] found that heating precipitated silica for 2 hours at about 1300° converted it partly into cristobalite. This was shown by an X-ray powder photograph of the product, which yielded lines identical with those given by cristobalite which had been made by melting water-glass with sodium phosphate, but less clear than those, presumably because of the diffuse radiation due to unchanged amorphous silica.

Endell and Rieke[18] found that amorphous precipitated silica was changed

[16] Article cited in IV, note [4].
[17] Article cited in X, note [20].
[18] Article cited in V, note [15].

completely into cristobalite by one heating in a porcelain kiln (18 hours above 1200°, maximum 1450°).

Houldsworth & Cobb heated their precipitated silica twice to 1170° and then measured its expansion. It expanded steadily to 100°, then about five times as rapidly to 200°, again at the original rate to 550°, finally contracting a little to 1000°. This curve suggests the presence of both cristobalite and tridymite.

When the amount of flux is increased considerably above that produced merely by the salt impurities, the changes are still further accelerated. Thus Fenner found that when precipitated silica was heated with sodium tungstate within the tridymite range, 870 to 1470°, it was partly changed into cristobalite, the rest going to tridymite, the stable phase.

The crystallization of micro-amorphous silica without the aid of water solutions was first accomplished by G. Rose,[19] who heated it with "salt of phosphorus" ($NaNH_4HPO_4.4H_2O$).

Rose's method was improved upon by Hautefeuille,[20] who heated amorphous silica with sodium tungstate and with lithium tungstate at about 960°, obtaining tridymite in thin hexagonal plates.

Hautefeuille & Margottet[21] obtained tridymite presumably from amorphous silica by heating it with LiCl at about 1000°.

Day, Shepherd & Wright[22] report the formation of "tridymite" direct from precipitated silica at temperatures above 1000°. The product was afterwards found to be cristobalite.

Below 870° quartz is the form to which amorphous silica readily crystallizes in the presence of solvents. Hautefeuille,[23] who was the first to prepare quartz in the laboratory without the aid of water solutions, obtained quartz crystals by heating "amorphous silica" (source not stated) with sodium tungstate and with lithium tungstate at 750°.

Hautefeuille & Margottet obtained quartz from silica,—presumably amorphous,—with lithium chloride, LiCl, as a molten flux, noting that the action was more rapid when oxychloride was present. Quartz was formed at temperatures "below the melting-point of silver" (960°), and the authors remarked that the temperature range within which quartz was obtained was wider in LiCl than in sodium and lithium tungstates. Since it is very improbable that they obtained quartz above 870° (where it would be an unstable phase), this probably means that quartz was obtained at lower temperatures in LiCl, or that they obtained some tridymite as an intermediate unstable phase below 870° in the tungstates but not in LiCl.

Precipitated silica, when heated with sodium tungstate at temperatures of 800 to 850° for several hours, crystallizes into tridymite, which then changes further into quartz, the stable phase.[24]

[19] Article cited in IV, note [23].
[20] Article cited in IV, note [5].
[21] HAUTEFEUILLE, P., & MARGOTTET, J., *Sur la silice et les silicates de lithine*, Bull. Soc. Mineral. Franc. (1881) **4**: 241-246; Compt. rend. Acad. Franc. (1881) **93**: 686-689.
[22] Article cited in V, note [3].
[23] Article cited in IV, note [5].
[24] FENNER, articles cited in IV.

Silica in the presence of water solutions

Micro-amorphous silica crystallizes to quartz also in the presence of water solutions at high temperatures, if below 870°.

Fenner produced a small proportion of perfectly-formed quartz crystals from precipitated silica by heating it with water and hydrofluoboric acid at 350 to 380° for 22 hours.

AN UNRECOGNIZED TRANSFORMATION IN MICRO-AMORPHOUS SILICA

By means of heating curves on precipitated silica, run at about 8° per minute, Houldsworth & Cobb [25] observed a heat evolution due to some permanent change, since it did not appear on subsequent reheating. With air-dried silica prepared from water-glass by precipitation with hydrochloric acid, the effect took place at 330 to 355° C. With pure amorphous silica prepared from silicon fluoride it took place at 365 to 405° C.

An irreversible heat evolution such as this suggests either (1) crystallization, (2) permanent change of structure without crystallization, or (3) some kind of sintering with reduction of surface. The data already presented show that these temperatures are far too low for true crystallization to cristobalite or tridymite. This leaves the possibilities (2) and (3) as explanations of the heat effect, but no further evidence has been obtained.

Powdered vitreous silica ("vitreosil") showed no thermal effects. The upper limit of temperature in these tests on silica is not stated, but was presumably about 1250°.

Historical notes on the crystallization of micro-amorphous silica

The early experiments of H. Rose [20] on the specific gravity of the silica obtained from various silicates are summarized below:

Source	Type	Dried	Specific gravity		
			Light ignition	Heated long time at white heat	Heated in porcelain kiln
Stilbite and HCl	Granular	2.145 *	2.190		2.206
Apophyllite and HCl	Gelatinous		2.218		2.22
Residues from silicate analyses			2.251		2.311
$SiF_4 + H_2O$				2.301	2.291
Infusorial earth (Lüneburger Haide)			2.224		2.303

* Dried at 150°, contains 4.85 per cent H_2O.

[25] Article cited in XI, note [5].
[20] Article cited in IV, note [12].

From the specific gravities given it is fairly certain that all these various types of micro-amorphous silica were converted into cristobalite by the high-temperature treatments, although Rose did not recognize the products as being crystalline, and tridymite and cristobalite had not yet been discovered.

Permutations (33) to (37): Production of micro-crystalline silica from other forms

By heating vitreous silica at 700 to 750° in the presence of mixed vapors of KCl and NaCl, Brun[27] produced a finely fibrous aggregate whose properties were not determined but which may have been an artificial chalcedony. Continued heating, totaling 40 hours, produced recognizable crystals of quartz. No systematic experiments have been made to determine what conditions encourage the production of a micro-crystalline instead of a coarsely crystalline product.

High-low inversions in the micro-forms

Chalcedony shows evidence of a high-low inversion extending over a range of temperature from about 575° down to some rather indefinite lower temperature, perhaps 525°. There are not yet data enough to say just what is the character of the inversion, but it is undoubtedly present in specimens of chalcedony from at least three different sources.

The experimental data

Our knowledge of the high-low inversion of chalcedony comes chiefly from thermal curves by Fenner and by White and heat capacity measurements by Wietzel.

Wietzel's data will be considered in Chapter XIX.

Fenner[28] made experiments on natural chalcedony from three localities: (a) Chihuahua, Mexico; (b) Kerguelen Island, in the South Indian Ocean; (c) Tampa Bay, Florida. Heating and cooling curves with a differential thermel, in the apparatus used to determine the inversion points of quartz, tridymite, and cristobalite (see Fig. V.2), showed no such sharp breaks as are characteristic of those inversions. In fact, the temperatures ran along so smoothly that it did not seem worth while to plot them, and Fenner reported in his original paper that chalcedony showed no quartz inversion.

When subsequent experiments and discussion had brought out the possibility that the inversion might be spread over a range of temperature, I obtained permission from Dr. Fenner to plot the original data, and found that the heating curves for chalcedonies (a) and (b) do show a slight change of direction beginning in the neighborhood of 520 to 530°, and ending near 580°. Three cooling curves on the same two specimens show a similar change of direction at 573 to 577°. The Tampa Bay specimen gave no satisfactory indications of any inversion phenomena on either heating or cooling.

As these results were hardly conclusive enough, White[29] made further tests

[27] Brun, A., article cited in VI, note [62].
[28] Fenner, C. N., p. 380 of article cited in IV, note [2].
[29] White, W. P., abstract note in Bull. Geol. Soc. Amer. (1924) **35**: 112.

with a more sensitive differential thermel, using chalcedony (a), and obtained definite evidence that there is an inversion which produces its maximum heat-absorption near 575°, although the effect is much less than that characteristic of quartz. The original experimental curves [30] are reproduced in Figure XI.2.

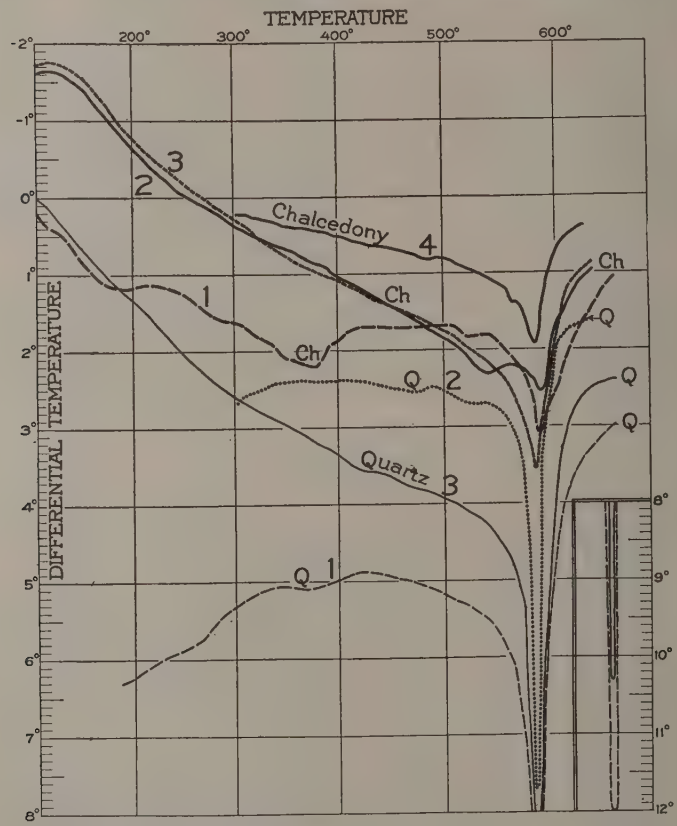


FIG. XI.2.—Differential time-temperature curves for quartz (Q) and chalcedony (Ch). Unpublished data by W. P. White.

A reasonable interpretation of the curves is that the absorption of heat due to high-low inversion in the chalcedony begins at a lower temperature and extends over a wider range than is the case in quartz, although it ends at about the same temperature as in quartz.

[30] Kindly furnished to me by Dr. WHITE.

A polished thin section of chalcedony (b) (Kerguelen Island), cut approximately parallel with the fibers, when heated and observed in the thermal microscope from below 100° up to 820°, showed no sudden change in birefringence at any temperature.[31] The same was true during cooling, down to 400°. These observations agree with the heating and cooling curves in indicating the absence of any such marked inversion point as is characteristic of quartz. But since the birefringence is small a slow change over a range of temperature might not have been detectable in this way.

Anhydrous chalcedony, when heated, often fractures[32] in the neighborhood of 600°. An inversion of the quartz type occurring near the temperature of the quartz inversion would explain this fracturing.

Lacroix[33] looked for a high-low inversion in his pseudo-chalcedonite at about 173°C, but found none.

Stein[34] states that he found a heat-effect in chalcedony at 173°. He made heating and cooling curves with a thermel on a charge of 250 grams of chalcedony, and repeated them 3 times with the same result. The absorption or evolution of heat held the temperature constant for 25 to 30 seconds.

This is a rather unexpected observation. No details as to the kind of thermel, its calibration, etc., are given and the accuracy cannot be judged. There is also no information about the source or previous history of the chalcedony. I suspect that it had previously been heated hot enough to convert it to cristobalite, and that the 173° observation is a low reading of the cristobalite inversion.

A 500-gram sample of flint from Helgoland gave no heat-effects at any temperature between 100 and 600° (Stein).

[31] Fenner, C. N., p. 380 of article cited in IV, note [2].
[32] Le Chatelier, H., article cited in VII, note [27].
[33] Lacroix, A., article cited in Tab. X.1.
[34] Article cited in VI, note [26].

Part 3. Symmetry and Structure

Chapter XII. SYMMETRY OF THE MODIFICATIONS

Symmetry

Every crystalline phase of a substance has a characteristic *symmetry* with reference to each of its directed properties. This symmetry must depend in the final analysis upon the arrangement and the systematic movements in space of the constituent parts of the substance,—electrons, atoms, atom-groups, molecules, molecule-groups. Symmetry is most obvious in the geometrical outline of freely-growing crystals of the substance, but it also crops out in the study of any properties which vary with the direction.[1]

Types of symmetry

It has been known for nearly one hundred years that there are 32, and only 32, possible types or *classes* of crystal symmetry. Their classification and nomenclature has varied with the point of view from which the subject has been presented or taught. Elementary instruction in crystallography as an aid to mineralogy is usually based, in effect, on the geometrical properties of solid wooden models, and the emphasis then comes on the classification of symmetries into six or seven *systems* with subordinate normal or holohedral (full-faced), hemihedral (half-faced), and tetartohedral (quarter-faced) classes. On the other hand, Groth's arrangement and nomenclature of the 32 symmetry classes, in which the emphasis on systems is secondary, are widely used in Europe and are followed in many English and American text-books of crystallography.

For convenience of reference there are brought together in Table XII.1 some of the classifications and designations in current use. The first and second columns give the classification and symbols employed by Schoenflies,[2] based on space-group theory (see XIII). The third column contains descriptive names of the classes, as used by Hilton[3] and other mathematical crystallographers. Usage here varies considerably; I have used names which give the table itself a kind of symmetry, rather than names which make a logically consistent system. The next two columns contain Groth's numbers and names, which are widely used. The final columns contain the numbers, names, and classification employed by Dana & Ford[4] in their well-known text-book.

[1] See Jaeger, F. M., *Lectures on the principle of symmetry,* (1917, Amsterdam) 333 pp.
[2] Schoenflies, A., *Theorie der Kristallstruktur* (1923, Berlin), p. 91.
[3] Hilton, H., *Mathematical crystallography* (1903, Oxford).
[4] Dana, E. S., & Ford, W. E., *Text-book of mineralogy* (1922, New York).

SYNONYMY OF THE 32 CLASSES OF CRYSTALLINE SYMMETRY.

Schoenflies	Hilton and others	Groth	Dana-Ford	
I Triclinic Syngony: C_1, S_2	Triclinic hemihedry	1. Asymmetric	32. Asymmetric	VI Triclinic System
	Triclinic holohedry	2. Pinacoidal	31. Normal triclinic	
II Monogonal Syngony: C_2, C_1^h, C_2^h	Monoclinic hemimorphous hemihedry	3. Sphenoidal	29. Monoclinic-hemimorphic	V Monoclinic System
	Monoclinic hemihedry	4. Domatic	30. Monoclinic-clinohedral	
	Monoclinic holohedry	5. Prismatic	28. Normal monoclinic	
III Digonal Syngony: V, C_2^v, V^h	Orthorhombic enantiomorphous hemihedry	6. Rhombic bisphenoidal	27. Orthorhombic-sphenoidal	IV Orthorhombic System
	Orthorhombic hemimorphous hemihedry	7. Rhombic pyramidal	26. Orthorhombic-hemimorphic	
	Orthorhombic holohedry	8. Rhombic bipyramidal	25. Normal orthorhombic	
IV Trigonal Syngony: C_3, C_3^i, D_3, C_3^v, D_3^d	Trigonal tetartohedry	16. Trigonal-pyramidal or ogdohedral	24. (No name)	III B Trigonal or Rhombohedral Division of Hexagonal System (Incl. Nos. 18 and 23, below)
	Hexagonal rhombohedral tetartohedry	17. Rhombohedral	21. Tri-rhombohedral	
	Rhombohedral enantiomorphous hemihedry	18. Trigonal-trapezohedral	22. Rhombohedral-trapezohedral	
	Rhombohedral hemimorphous hemihedry	20. Ditrigonal-pyramidal	20. Rhombohedral-hemimorphic	
	Rhombohedral holohedry	21. Ditrigonal-scalenohedral	19. Rhombohedral	
V Tetragonal Syngony: S_4, V^d, C_4, D_4, C_4^h, C_4^v, D_4^h	Tetragonal sphenoidal tetartohedry	9. Tetragonal-bisphenoidal	12. Tetragonal-tetartohedral	II Tetragonal System
	Tetragonal sphenoidal hemihedry	11. Tetragonal-scalenohedral	10. Tetragonal-sphenoidal	
	Tetragonal tetartohedry	10. Tetragonal-pyramidal	9. Tetragonal-pyramidal-hemimorphic	
	Tetragonal enantiomorphous hemihedry	12. Tetragonal-trapezohedral	11. Tetragonal-trapezohedral	
	Tetragonal paramorphous hemihedry	13. Tetragonal-bipyramidal	8. Tetragonal-pyramidal or -tri-pyramidal	
	Tetragonal hemimorphous hemihedry	14. Ditetragonal-pyramidal	7. Tetragonal-hemimorphic	
	Tetragonal holohedry	15. Ditetragonal-bipyramidal	6. Normal tetragonal	
VI Hexagonal Syngony: C_3^h, D_3^h, C_6, D_6, C_6^h, C_6^v, D_6^h	Hexagonal sphenoidal tetartohedry	19. Trigonal-bipyramidal	23. (No name)	(To III B above)
	Hexagonal sphenoidal hemihedry	22. Ditrigonal-bipyramidal	18. Trigonal or trigonotype	
	Hexagonal tetartohedry	23. Hexagonal-pyramidal	16. Hexagonal-pyramidal-hemimorphic	III A Hexagonal Division of Hexagonal System
	Hexagonal enantiomorphous hemihedry	24. Hexagonal-trapezohedral	17. Hexagonal-trapezohedral	
	Hexagonal paramorphous hemihedry	25. Hexagonal-bipyramidal	15. Tripyramidal	
	Hexagonal hemimorphous hemihedry	26. Dihexagonal-pyramidal	14. Hexagonal hemimorphic	
	Hexagonal holohedry	27. Dihexagonal-bipyramidal	13. Normal hexagonal	
VII Cubic Syngony: T, O, T^h, T^d, O^h	Regular tetartohedry	28. Tetrahedral-pentagondodekahedral	5. Isometric-tetartohedral	I Isometric System
	Regular enantiomorphous hemihedry	29. Pentagon-icositetrahedral	4. Isometric-plagiohedral	
	Regular paramorphous hemihedry	30. Dyakisdodekahedral	2. Isometric-pyritohedral	
	Regular hemimorphous hemihedry	31. Hexakistetrahedral	3. Isometric-tetrahedral	
	Regular holohedry	32. Hexakisoctahedral	1. Normal isometric	

Determination of symmetry

A crystalline substance may grow under such conditions that it develops no detectable plane faces. This is commonly the case with the minerals of igneous rocks, including quartz and tridymite. The material is then called *anhedral* and its shape may give no indication of its true symmetry.

Conditions can usually be found, however, which permit the substance to develop with visible plane faces and straight edges. Such material is called *euhedral*. It is an experimental fact, supported now by thousands of measurements, that the angles between geometrically similar faces of euhedral crystals of a given substance are always the same, no matter how misshapen the crystal fragment may appear to be.

A mere inspection of the faces, growth-forms, and etch-figures (see XXV) may be sufficient to establish the crystallographic system in which the substance belongs, while a more careful study of the geometry of the forms and a measurement of the angles is usually sufficient to establish definitely its symmetry class.

The symmetry class of both anhedral and euhedral material may also be determined with reference to its optical, elastic, thermal, electric, or magnetic properties.

In general, the symmetry of a substance with respect to these various properties is found to be concordant with that shown by its euhedral crystal-forms, and the latter symmetry is therefore usually referred to as *the* symmetry of the substance. It should be noted, however, that some property not yet examined may reveal a different degree of symmetry from that revealed by the other properties, so that a crystalline substance is always subject to the risk, so to speak, of being found to have a lower degree of symmetry, at least with reference to the property examined, than it has hitherto been supposed to possess.

Symmetry revealed by X-rays

The most searching means of finding out the fundamental symmetry of a substance is by means of X-rays. The wave-length of the radiation from the target of an X-ray tube is of the same order of magnitude as the spacing of the atoms in a crystal, so that the atomic pattern affects the X-radiation in a manner similar to the effect of a diffraction grating upon visible light. The X-rays are diffracted at definite angles, which can be measured by allowing the rays to impress a photographic plate or ionize a gas. It is then possible to obtain information as to the actual distribution of the atoms in space from the angles and the intensities of the diffracted rays.

This method of investigation will be considered further in Chapter XIII.

Symmetry of the crystalline modifications of silica

The principal crystallographic data on the modifications of silica are given in Table XII.2.

Table XII.2.

Crystallographic Symmetry of the Modifications of Silica.

Modification	Symmetry system	Symmetry class		
		Schoenflies	Groth	Dana
Low-quartz	Hexagonal; rhombohedral or trigonal subdivision	Trigonal enantiomorphous hemihedral D_3	Trigonal trapezohedral	Rhombohedral-trapezohedral
High-quartz	Hexagonal; hexagonal subdivision	Hexagonal enantiomorphous hemihedral D_6	Hexagonal trapezohedral	Hexagonal-trapezohedral
Low-tridymite	Orthorhombic			
Lower high-tridymite	Hexagonal	(A hemihedral class?)		
Upper high-tridymite	Hexagonal	(A holohedral class?)		
Low-cristobalite ...	Either tetragonal or orthorhombic			
High-cristobalite ..	Isometric			

The symmetry of quartz

Low-quartz is the most important and most familiar example of the "trigonal enantiomorphous hemihedral" or *trigonal trapezohedral* class of symmetry. This class is characterized by one axis of threefold symmetry, with 3 axes of twofold symmetry perpendicular thereto and separated by angles of 120°, as illustrated in Figure XII.1.

An axis of threefold symmetry is a line about which a structure or object can be rotated through one-third of a complete turn without any change in appearance when the rotation is complete, so that an observer who had not seen the actual motion would be unable to tell that any rotation had taken place. Similarly, an axis of twofold symmetry is one about which the structure can be given one-half of a complete turn without leaving any recognizable trace of the rotation.

This class has no plane of symmetry and no center of symmetry.

Crystals of substances belonging to this class are usually described with the aid of the following crystallographic conventions:

(1) A "vertical axis" or *principal axis* is assumed, whose direction coincides with that of the axis of threefold symmetry. This axis is designated by *c*.

(2) Three "horizontal," "secondary," or *equatorial* axes are assumed, coinciding in direction with the three axes of twofold symmetry. These are designated by *a*.

(3) The positive direction of *c* is assumed to be upwards.

(4) The positive directions of the three *a* axes are taken thus: a_1, toward the front, to the left; a_2, to the right, perpendicular to the observer's line of sight; a_3, toward the back, to the left.

These conventional axes are shown in Figure XII.2.

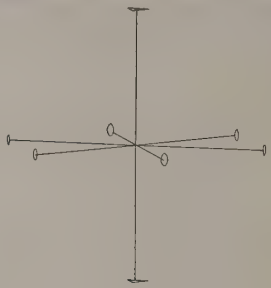


Fig. XII.1.

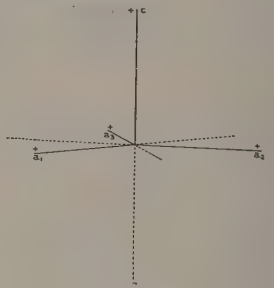


Fig. XII.2.

Fig. XII.1.—Elements of symmetry of the trigonal trapezohedral class.

Fig. XII.2.—Conventional crystallographic axes used in describing a crystal of a substance having either trigonal trapezohedral symmetry, such as low-quartz; or hexagonal trapezohedral symmetry, such as high-quartz.

On these conventional axes as a frame various geometrical *crystal-forms* can be constructed. Each crystal-form is built by setting up a plane so that it intersects one or more of the four axes at measured distances from the common axial intersection, and then putting this plane through the symmetry operations of the class; namely, three rotations of 120 degrees each about the principal axis, and two rotations of 180 degrees each about each of the equatorial axes. Each plane so treated yields a crystal-form,[5] and these forms serve to describe the correspondingly situated forms on an actual crystal of quartz.

These planes may not be chosen at random, however. There is an important law governing the dimensions of the forms of the actual substance. It is a fact of observation that the intercepts of the planes of

[5] Note the distinction between "crystal-form," a geometrical concept, and the "crystalline forms" or crystalline polymorphous modifications described in Chapter IV.

actual crystal-forms on a given axis stand in the relation to one another of *small* whole numbers. This fact is called the *law of the rationality of indices.*

These whole-number intercepts serve to designate the plane from which the form is derived as well as all the other planes which make the faces of the form. The most generally used method is to employ the reciprocals of the intercepts, since the reciprocals also are in the relation of small whole numbers. These are the *Miller-Bravais indices.* They are written conventionally in the order $a_1\ a_2\ a_3\ c$. A negative index is written with the minus sign over the figure.

The symbol for a single plane or face is usually written in parentheses, thus: $(10\bar{1}1)$. The symbol for the form as a whole is the symbol of a face written in brackets, thus: $\{10\bar{1}1\}$.

From the geometry of the conventional axes it follows that the sum

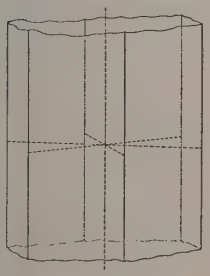


FIG. XII.3.

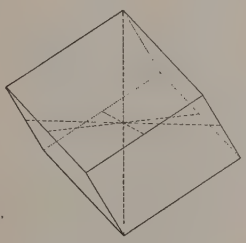


FIG. XII.4.

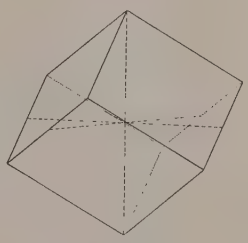


FIG. XII.5.

FIG. XII.3.—The first-order hexagonal prism, $\{10\bar{1}0\}$.
FIG. XII.4.—The primary positive first-order rhombohedron of low-quartz, $\{10\bar{1}1\}$.
FIG. XII.5.—The primary negative first-order rhombohedron of low-quartz, $\{01\bar{1}1\}$.

of the first three indices is always zero. Only three out of the four are truly independent.

Application to low-quartz

The usual crystal of quartz may be crudely described as a distorted prism with a pointed tip. It is fitted to the conventional axes thus:

(1) Set the prism upright, so that the prism edges are parallel to the direction c.

(2) On the tip will usually be found three faces, equally spaced around the axis, which are larger and smoother than the other terminal faces. Turn the crystal around the vertical axis c until one of these three faces is parallel to a_2.

The position of the crystal is now fixed with reference to the conventional axes and the description of all its forms and of the forms of any other quartz crystal is a matter of geometry.

The many crystal-forms which have been observed on quartz wil receive further mention in Chapter XXV. For the present we shall consider only the simple geometry of these crystal-forms to show their accordance with the accepted symmetry of quartz.

Geometrical crystal-forms in the class of low-quartz

Forms which are of normal trigonal symmetry but not specially characteristic of the trigonal trapezohedral class are:

(A) A hexagonal prism with its front face perpendicular to the observer's line of sight. This is called the *first-order prism.* Symbol {10$\bar{1}$0}. See Figure XII.3.

(B) A rhombohedron with its upper front face toward the observer (tha is, parallel to a_2); called the *positive first-order rhombohedron.* There may b

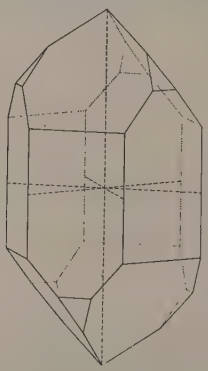


FIG. XII.6.—A combination of the three forms of Figures XII.3, XII.4, and XII on an imaginary crystal of low-quartz.

several such rhombohedrons, having different intercepts. One of them, adopte as standard for the substance, and characterized in the case of quartz by i making an angle of 141° 47′ with the prism face lying directly below it, called the primary positive first-order rhombohedron and has the symb {10$\bar{1}$1}. See Figure XII.4.

(C) A rhombohedron turned 60° about the vertical axis with respect the preceding; called the *negative first-order rhombohedron.* The primary o has the symbol {01$\bar{1}$1}. See Figure XII.5.

Figure XII.6 shows a combination of the three in an imaginary cryst The axial ratio adopted for the rhombohedrons is that of quartz, 1.1 (s p. 202).

(D) A basal plane, perpendicular to the principal axis. Symbol {0001 This form is seldom, if ever, found on quartz.

The trigonal trapezohedral symmetry class, to which low-quartz b longs, has the quality of *enantiomorphism.* This is the name given to t

relation between two objects which are similar but not superposable,—the relation between our right and left hands, or between an object and its image in a mirror.

This enantiomorphism is expressed in the geometry of the class by the existence of two groups of crystal-forms, called respectively *right-handed* and *left-handed.* The following are such forms; they are characteristic of the class:

(E) An equiangular triangular prism with one face perpendicular to the front face of the first-order hexagonal prism of Figure XII.3. If the edge opposite the face of the triangular prism just mentioned is turned to the right, it is called the "right trigonal prism of the second order" or simply the *right trigonal prism* $\{11\bar{2}0\}$; if the edge is to the left, it is the *left trigonal prism* $\{2\bar{1}\bar{1}0\}$.

(F) A type of six-sided prism which may be considered as produced by the extension of alternate pairs of faces of the holohedral dihexagonal prism.

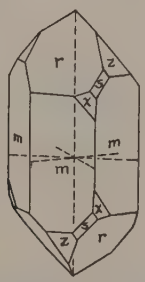


FIG. XII.7.—Crystal of right-low-quartz, showing pyramid (s) and trapezohedron (x), in addition to the hexagonal prism (m), positive rhombohedron (r) and negative rhombohedron (z).

If the first pair used for extension lies to the right of the line of sight, the product is a *right ditrigonal prism;* if to the left, a *left ditrigonal prism.* General symbols, $\{hi\bar{k}0\}$ and $\{ki\bar{h}0\}$.

(G) A type of triangular pyramid which fits the ends of the trigonal prism (E). The pyramid is correspondingly called a "right trigonal bipyramid of the second order" or simply a *right trigonal bipyramid;* and there is a corresponding *left trigonal bipyramid.* General symbols, $\{h.h.\overline{2h}.l\}$ and $\{2h.\overline{h}.\overline{h}.l\}$.

(H) A type of six-sided trapezohedron which may be considered as produced by the extension of every fourth face,—alternately above and below,—of the holohedral dihexagonal pyramid. It is evident that there are four such *trigonal trapezohedrons.* The one which begins with the extension of the upper face to the right of the line of sight, followed by the face below and to the right, is called the *right positive trapezohedron;* the one which begins with the extension of the upper face to the left followed by the face below and to the left, is called the *left positive trapezohedron.* The corresponding

forms beginning 60 degrees farther around to the right or left, respectively, are called the *right negative trapezohedron* and the *left negative trapezohedron*. General symbol $\{hikl\}$.

The geometrical enantiomorphism just referred to is materialized in the face development of quartz crystals. Some natural crystals of quartz have small trapezohedral faces adjoining the lower *right*-hand corner of the positive rhombohedral faces, while others have these same small trapezohedral faces situated to the *left*. The one type of crystal cannot be transformed into the other by any procedure which does not cause the intermediate disappearance of crystallinity. The two kinds are called, respectively, "right-handed low-quartz" and "left-handed low-quartz," and will usually be referred to in this book as *right-quartz* and *left-quartz*.

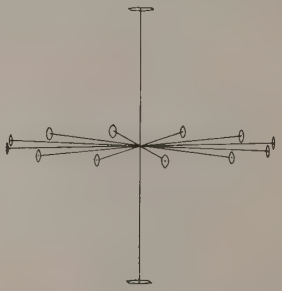


FIG. XII.8.—Elements of symmetry of the hexagonal trapezohedral class.

A combination of forms often seen on quartz and revealing its rightness or leftness is that shown in Figure XII.7. x is a positive trapezohedron, having the symbol $\{5\bar{1}61\}$ for the right-handed form; and s is a trigonal bipyramid, having the symbol $\{11\bar{2}1\}$ for the right-handed form.

The axes of the class of low-quartz

The three twofold symmetry axes, being perpendicular neither to a symmetry-plane nor to an even-fold axis of symmetry, are *polar* axes. This name expresses the fact that certain properties of quartz differ according to the direction in which an investigator studying the phenomena may be imagined to be traveling along such an axis. The direction away from the observer is not equivalent to the direction toward the observer.

The three directions which bisect the angles between a_1, a_2 and a_3 are sometimes called *intermediate axes*. They are used,—and called "axes,"—merely for purposes of convenient description; they are neither crystallographic reference axes nor axes of symmetry.

High-quartz

The symmetry of high-quartz is hexagonal, contrasting with low-quartz, which is trigonal. The symmetry class is *hexagonal trapezohedral.*

The hexagonal trapezohedral class (see Table XII.1) is characterized by one sixfold axis of symmetry, and 6 twofold axes perpendicular thereto and separated by angles of 30°, as shown in Figure XII.8. As with low-quartz, there is no plane of symmetry and no center of symmetry.

In describing a hexagonal crystal, such as high-quartz, the same conventional crystallographic axes are used as have been described for low-quartz (see Figure XII.2). The axes are referred to as the vertical or *principal* axis *c,* and the three horizontal, secondary, or *equatorial* axes *a.* These equatorial crystallographic axes are made to coincide with three of the twofold symmetry axes.

The hexagonal trapezohedral class is like the trigonal trapezohedral in having the geometrical property of enantiomorphism, so that right-handed and left-handed crystals are possible. The crystal derived by high-low inversion from a right-handed crystal of low-quartz is *right-handed high-quartz,* which may be abbreviated to right-high-quartz; and the crystal derived from left-low-quartz by the high-low inversion is left-high-quartz.[5a]

The only crystal-forms betraying the geometrical enantiomorphism of the class are the *hexagonal trapezohedrons,* of which there is one right and one left, each having 12 faces. All of the other crystal-forms of this class are holohedral hexagonal forms.

Experimental evidence on the symmetry of high-quartz

If we had to judge solely by the fact that quartz maintains its general hexagonal symmetry when inverting from low to high, and by the persistence of its axis and of its optical rotatory power, we might place high-quartz in any one of four symmetry classes: (1) It might remain trigonal trapezohedral after the inversion, with only a change of axial ratio; or it might become (2) hexagonal pyramidal, (3) trigonal pyramidal, or (4) hexagonal trapezohedral.

The choice among these classes has depended almost entirely on the study of etch-figures and twinning phenomena.

The general hexagonal symmetry of high-quartz was first shown in 1902 by Friedel[6] who etched a crystal at 600° in potassium acid sulfate containing potassium fluoride, and found that the etch-figures on what had been the rhombohedral faces of low-quartz were all alike and similarly oriented. (See Chapter XXV.)

[5a] This is the relation normally to be expected, but it is not necessary geometrically, nor can I refer to any rigid experimental proof of it. The crystal-forms assumed by high-quartz are usually holohedral in character and reveal nothing about rightness or leftness. Rightness and leftness in optical rotatory power is logically an independent matter (see p. 648).

[6] FRIEDEL, G., *Sur les figures de corrosion du quartz à haute température,* Bull. Soc. Franc. Mineral. (1902) **25**: 112-113.

These observations do not of themselves decide the symmetry class of high-quartz. In fact, as Mügge[7] showed subsequently, the same kinds of etch-figures as those found by Friedel are obtained on low-quartz in potassium acid sulfate a little *below* 573°.

Mügge's etch-figures with sodium metaphosphate were likewise not sufficient to decide the question. They indicated that the twofold symmetry axes of low-quartz persist as twofold axes in high-quartz, which would eliminate the possibility of its being hexagonal pyramidal, but would still leave it possible for high-quartz to belong to one of the enantiomorphous classes of lower symmetry than hexagonal trapezohedral, namely, either trigonal pyramidal or trigonal trapezohedral.

Mügge's principal appeal, therefore, was to the twinning phenomena at the inversion-point, which will be considered on a later page. The net result of the study of twinning was to show that high-quartz is very probably hexagonal trapezohedral with an unlikely possibility that it might be hexagonal pyramidal.

Etching experiments by Nacken[8] furnished the final proof that the symmetry class of high-quartz is hexagonal trapezohedral. Nacken used small spheres which were etched in sodium metaphosphate at about 700°. The patterns thus developed showed the symmetry much more clearly than did the etch-figures on polished plates of quartz.

The change from trigonal to hexagonal symmetry at the inversion-point is brought out very clearly by the change with temperature of Young's modulus of elasticity, as measured by Perrier & Mandrot.[9] In addition to making measurements parallel to the threefold and twofold axes of low-quartz, they cut two plates to give values of the modulus in directions perpendicular to a twofold axis but at $+50°$ and $-50°$, respectively, to the threefold axis. These two directions are not equivalent in low-quartz and the two moduli are very different. Above the inversion temperature, however, the two are the same within the error of measurement, showing that the elastic symmetry of high-quartz is a symmetry of revolution as it should be for a hexagonal crystal.

Other properties of high-quartz which are in agreement with hexagonal trapezohedral symmetry are the absence of piezo-electricity,[10] and the symmetry of Laue X-ray photographs of quartz above 573°, as made by Gibbs, Rinne & Gross,[11] and others.

Crystallographic relations between low-quartz and high-quartz

When a fragment of low-quartz inverts at 573° into high-quartz the axis of threefold symmetry remains fixed in direction. The 3 twofold axes of the low-quartz change into 3 of the 6 twofold axes of the high-quartz. Finally, all of the plane faces on the low-quartz remain as plane faces on the high-quartz. The crystallographic axes of Figure XII.2 may there-

[7] Mügge, O., article cited in VII, note [3].
[8] Nacken, R., *Ätzversuche an Kugeln aus Quarz und α-Quarz,* Neues Jahrb. Min. etc. 1916, I: 71-82, pls. 10-11.
[9] Perrier, A., & Mandrot, B. de, Compt. rend. Acad. Paris (1922) **175**: 622-624.
[10] Perrier, A., article cited in VII, note [10].
[11] Mügge, O., Centr. Mineral. etc. 1921: p. 609.

fore be considered to remain unchanged in position. The same relations hold true for the reverse inversion.

Geometrically, then, the inversion at 573° is simply a change from tetartohedral (quarter-faced) to hemihedral (half-faced) symmetry, the structure as a whole remaining hexagonal in the general sense. The axial ratio and the volume are altered at the same time, to be sure, but those changes are specific changes in shape and dimensions and do not affect the general geometry of the two modifications.

Historical notes on the symmetry of quartz

Silica has played a prominent part in the development of our knowledge of the structure of matter, especially of matter in the crystalline state.

Silica in the form of quartz crystals was a familiar substance to the early students of inorganic science. It was their "crystal" *par excellence,* supposed to be a permanent and unmelting form of ice (Greek Κρύσταλλος, Latin *crystallus*). It was the substance with which Niels Stensen (Steno) in 1669 gave the initial impulse to the science of crystallography, by showing that the angle between corresponding faces on different specimens is a constant, characteristic of the substance. It also had a prominent place among the crystals with which Haüy and Romé de l'Isle laid the foundations of modern mineralogy.

The existence of two enantiomorphous growth-forms on quartz was first observed by Herschel,[12] in 1821. He was led to look for them through speculations as to the cause of the optical rotatory power of quartz, which had been discovered by Biot in 1813.

Biot had recognized that there are two kinds of quartz, having the power to rotate the plane of polarization in opposite directions, but not differing in any other way that he could observe.

Brewster,[13] studying the optical properties of amethyst, noted that Biot's two varieties of quartz were intimately intergrown in some portions of his amethyst crystals, and ventured the prediction that corresponding differences in external form would be found.

This prediction was fulfilled by Herschel, working independently at about the same time, who found that crystals of quartz of the variety or habit which Haüy had called "plagièdre" can be sorted into two groups, having plagihedral (trapezohedral) faces "leaning opposite ways."

Haüy had, to be sure, observed the fact that the trapezohedral face always occurs at one side of the rhombohedral face and not at both sides, but his illustrations always show the trapezohedral face at the *right.* He apparently failed to observe that it may occur also at the left.

Herschel then found further that the two kinds of quartz give opposite optical rotations, and confirmed this fact on 23 different specimens.

[12] Herschel, J. F. W., *On the rotation impressed by plates of rock crystal on the planes of polarization of the rays of light, as connected with certain peculiarities in its crystallization,* Trans. Cambridge Phil. Soc. (1821) 1: 43-52.

[13] Brewster, D., *On circular polarization, as exhibited in the optical structure of the amethyst . . .,* Trans. Roy. Soc. Edinburgh (1823) 9: 139-152. (Presented in 1819.)

From Herschel's description of the optical properties it appears that the kind of crystal which he called "left-handed" is the kind now generally known as right-handed.

The existence of enantiomorphous right and left forms was independently discovered by the crystallographer Weiss in 1836. Herschel had made the direction of the optical rotation his criterion for the naming of right-handed and left-handed varieties. Weiss, on the contrary, adopted the purely geometric criterion as the basis for his names. The combination of the trapezohedron *x* and the pyramid *s* with the rhombohedron and prism on the crystal shown in Figure XII.7 guides the eye from the upper right-hand side of the crystal downward toward the left. This is the direction of slope as we look at the threads of an ordinary wood-screw or machine-screw, of the kind which we turn "right-handed" (clockwise) as we drive it into its socket, and which we accordingly call a "right-handed screw." Weiss therefore called such a quartz crystal a "rechtsgewundenen Krystall," and called the opposite kind "links-gewundenen" (right-twisted and left-twisted). This convention as to the rightness and leftness of the geometrical forms is still in use.

Twinning

The symmetries just described all refer to homogeneous *untwinned* material, that is, silica in units which are easily visible and which have properties that are perceptibly constant along any given direction. But the external symmetry is often complicated by the structural phenomenon known as *twinning.*

"Twinning" is the name given by crystallographers to a structural habit shown by many crystalline substances, whereby one or more portions of a crystal are reversed in position with reference to other portions. In the more restricted sense which accords with the derivation of the word, "twinning" refers to *two* similar crystals, or two individual portions which may be considered halves of one crystal, which are so united that they are symmetrical with reference to some plane which is not a symmetry-plane of either portion alone. This plane is called the *twinning-plane.* In most cases, but not all, the two halves are in relative positions which might have been attained by the rotation of one of the halves about an axis which is perpendicular to a possible face. This axis is called the *twinning-axis.*

Twinning in quartz

Low-quartz exhibits two principal types of twinning.

The first type may be imagined as having been produced by turning one portion of a crystal 180° about an axis, and then reuniting it with the other portion, which has stood still. This type is called [14] the *orientational.*

The second type can not be produced by any physical rotation of parts.

[14] Kelvin, *Baltimore lectures* (1904) p. 640.

One portion is the mirror image of the other, and the two halves are no more interchangeable than two gloves. This is the *chiral* type.[15]

The principal examples of these two types are:

Orientational type: *Dauphiné twin.* The two portions of the crystal are of the same kind (both right-handed or both left-handed), but one is rotated 180° about the principal axis with respect to the other. In other words, the twinning-axis is *c*. The twinning-plane is a face of the first-order hexagonal prism.

Chiral type: *Brazil twin.* The two crystalline individuals are of opposite kinds, one being right-handed, the other left-handed, with a face of the trigonal prism of the second order $\{11\bar{2}0\}$ (at 30° to the common prism face) as twinning-plane. Since one is not derivable from the other by any rotation, there is no twinning-axis.

A less common twin of the orientational type is the *Japanese twin.* The

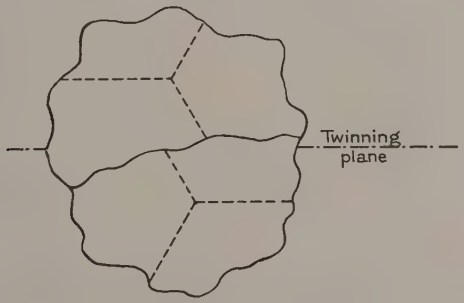


FIG. XII.9.—Diagram to illustrate the production of a Dauphiné twin at the inversion-point of quartz.

two portions are symmetrical with respect to a trigonal bipyramid of second order, namely, the pyramid $\{11\bar{2}2\}$ on a right-handed crystal, or the pyramid $\{2\bar{1}\bar{1}2\}$ on a left-handed crystal.

Several other styles or habits of twinning in quartz are on record, but need not be described here in detail.[15a] Their geometry and interrelations have recently been thoroughly reviewed by Friedel.[16]

TWINNING RELATIONSHIPS BETWEEN HIGH-QUARTZ AND LOW-QUARTZ

It has been found experimentally that the twofold symmetry axes of low-quartz remain twofold axes when it inverts into high-quartz, and conversely. But the inversion from high-quartz to low offers a choice of axes that is absent in the inversion from low to high.

[15] KELVIN also employed a term used by the French mineralogists, and called twinning "macling," but this term has never come into general use.

[15a] See NIGGLI, P., *Lehrb. Mineralogie* (1926, Berlin) II: p. 420.

[16] FRIEDEL, G., *Sur les macles du quartz,* Bull. Soc. Franc. Min. (1923) **46**: 79-95.

Suppose the inversion to commence simultaneously at two different points in the crystal. The new twofold axes of the low-quartz coincide with those twofold axes of the high-quartz which form the crystallographic axes; but the *polarity* is still to be decided. The three twofold axes of low-quartz are polar, and it makes a difference which way they are directed. It is geometrically an even chance that they will be directed oppositely in the two hypothetical inverting portions of the crystal, and the result will be a Dauphiné twin, having as twinning-plane the first-order prism (10$\bar{1}$0). (See Figure XII.9.)

The experimental facts fully meet this expectation, as Mügge [17] first showed. If a plate of quartz be first tested by etching to prove its homogeneity, then repolished, heated to above 573°, cooled, and etched again,

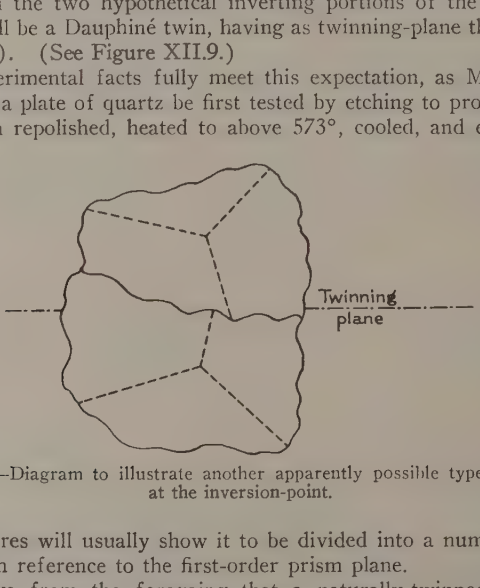


FIG. XII.10.—Diagram to illustrate another apparently possible type of twinning at the inversion-point.

the etch-figures will usually show it to be divided into a number of areas twinned with reference to the first-order prism plane.

It follows from the foregoing that a naturally-twinned low-quartz crystal of the Dauphiné type should be converted by the inversion at 573° into an untwinned crystal, and that on inverting back during cooling it should become twinned again according to the same law, but in units having different boundaries from the original. The phenomena observed are all in agreement with this expectation.

So far as the symmetry is concerned, the net result of the inversion of low-quartz to high-quartz is exactly what would be attained by starting with the low-crystal in the form of a twin of the Dauphiné type (that is, both individuals right-handed or both left-handed) and making the twinning more and more intimate,—the individual homogeneous portions smaller and smaller,—until the separate individuals were no longer distinguishable, even with the microscope. The resulting submicroscopically twinned crystal would be, to all appearances, hexagonal trapezohedral, like

[17] MÜGGE, O., article cited in VII, note [3].

a crystal of high-quartz. Whether or not it would *be* high-quartz is another question, to be considered further under the theory of the structure and the energy-properties.

In the inversion from high-quartz to low, another choice, besides that of polarity, might theoretically be possible. There are six twofold axes in high-quartz, and three of them must be selected in preference to the other three when the high-quartz inverts. Suppose, as before, that the inversion commences simultaneously at two different points in the crystal; it might seem at first sight to be an even chance that the threefold axes of the two inverted portions would be set at an angle of 30° instead of being parallel, whence the two portions would be twinned, the twinning-plane being a prism set at an angle of 15° to the hexagonal prism. (See Figure XII.10.)

The six twofold axes of high-quartz can not, however, all be equivalent as regards their possibilities upon inversion; they must fall into two groups, at 30° to one another. It is not an even chance that the inversion may start at two distinct points with axes at 30°. The odds must be either for or against this occurrence, by an amount which is unpredictable without additional experimental information or additional knowledge of the mechanism of the inversion. Furthermore, the imaginary twinning-plane shown in Figure XII.10 is not a plane having rational indices; it is not a possible face of low-quartz. Therefore, even if the assumed choice of axes did happen, it would not result in twinning.

In determining the symmetry-class of high-quartz Mügge[18] considered the possible twinning phenomena of several classes. In addition to the hexagonal trapezohedral, which has already been discussed in preceding pages, there are three other classes (see Table XII.1) to which there is a possibility that high-quartz might belong. They are: (a) trigonal trapezohedral, (b) trigonal pyramidal, (c) hexagonal pyramidal.

(a) If it were trigonal trapezohedral, the same class as low-quartz, then no twinning could be expected at the inversion, either on rising or falling temperature.

(b) If it were trigonal pyramidal, it would have only one axis of threefold symmetry, which is polar, and no other elements of symmetry. A crystal of low-quartz in changing into high-quartz might then change into two crystals having axes directed oppositely. On changing back, the simplest supposition is that it would be restored to its original constitution. Further, a natural Dauphiné-twinned crystal, after having been through the inversion and back again, might be expected to regain its original twinning boundaries unchanged.

(c) If it were hexagonal pyramidal, it would have only an axis of sixfold symmetry, which is polar. As in the preceding case, a crystal of low-quartz might therefore change into two portions having oppositely-directed axes, which would again reunite on cooling; but in addition there would be the possibility found with the hexagonal trapezohedral class, of a choice of polarity in a horizontal direction, resulting in Dauphiné twinning on the reverse in-

[18] Article cited.

version, or, if such twinning were already present, in a change of the twinning boundaries.

The phenomena predicted under (a) and (b) do not occur, from which it follows that high-quartz is not of either of these two classes. The Dauphiné twinning predicted under (c) does occur, and on this basis alone high-quartz might belong to the hexagonal pyramidal class. Other evidence, however, makes its assignment to this class improbable.

Historical notes on twinning in quartz

The common or orientational type of twinning in crystalline substances, consisting in a simple rotation of one individual with respect to the other, was known to Haüy and Romé de l'Isle, the founders of modern mineralogy,

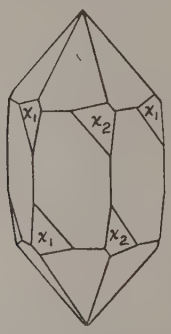


FIG. XII.11.

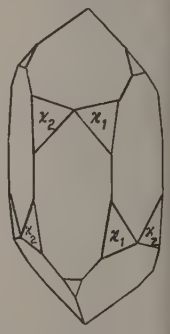


FIG. XII.12.

FIG. XII.11.—External appearance of an interpenetration twin of right-quartz, of Dauphiné type (orientational), showing the common trapezohedron (x).

FIG. XII.12.—External appearance of an interpenetration twin of right- and left-quartz, of Brazil type (chiral), showing the common trapezohedron (x).

before the year 1800, but they had not observed twinning in quartz. They were apparently not acquainted with that kind of twinned crystal in which the twinning-plane is not evident in the external form, nor did they know of the possibility of chiral twinning, where one individual is the mirror image of the other. Hence they must have had difficulties with quartz crystals of the kind shown in Figure XII.11 (orientational twin). If the faces x_1 fitted in well with the law of "integral decrements," x_2 would not fit so simple a formula. We now know that x_2 belongs to a different individual whose relation to the crystal bearing the face x_1 involves a rotation of 180°, so that, naturally, the indices of x_2 referred to the axes of x_1 would seem exceptional.

Twinning in quartz was first placed on record by Weiss[19] in 1816. He described and figured clearly the orientational type of quartz twins. The chiral type he appears also to have observed, though rarely, but spoke of it

[19] WEISS, C. S., *Ueber den eigenthümlichen Gang des Krystallisations-systemes beim Quarz, und über eine an ihm neu beobachtete Zwillingskrystallisation,* Ges. Nat. Freunde Mag. Berlin (1816) 7: 163-181, pl. 4.

cautiously as a kind of intergrowth which might possibly be explained as a case of twinning allied to the orientational. The difficulty was simply that the important difference between the two alternative choices,—positive versus negative forms on the one hand, and right versus left on the other,—had not yet been made clear.

Herschel[20] happened upon some twinned crystals in the course of his pioneer work on the correlation of optical activity and face development in quartz (see XXXIII), and was puzzled to find one specimen which had trapezohedral faces perfectly distinct and in contact but "tending opposite ways around the summit." Unfortunately it was "in the possession of Mr. Brooke," and Mr. Brooke apparently valued it too highly to let it be damaged in the interest of science, so Herschel was not allowed to section it and test its rotatory power for polarized light. The sympathy of every true mineral collector will be with Mr. Brooke, even though he did postpone an important scientific discovery for twenty-five years.

The explanation for this peculiar crystal was not forthcoming until G. Rose[21] published his comprehensive work in 1846. He was the first to show that the apparently homogeneous crystal with the opposite-tending faces is really a compound crystal, twinned according to the so-called Brazil law. (Fig. XII.12.)

The crystallographer Naumann believed that it is possible for both right and left trapezohedral forms to occur on the same homogeneous crystal unit of quartz, and in support of this opinion cited an occurrence of quartz in Brazil, consisting of small crystals which were apparently simple and which had as one of their bounding forms a complete scalenohedron, which would be a combination of right and left forms of the same (first) order. Groth[22] showed, by measurement of the rotatory power of a thin section, that these apparently perfect crystals are really twins, and are no exception to the general law.

The symmetry of tridymite

The symmetry of low-tridymite is almost certainly orthorhombic. The orthorhombic system includes 3 classes: the bisphenoidal, the pyramidal, and the bipyramidal. It is not known to which of these classes low-tridymite belongs.

Upper high-tridymite is of hexagonal symmetry, and the absence of any large change in optical properties at 163° indicates that lower high-tridymite is of a symmetry identical or closely allied with that of the upper high-modification. It is very probable, therefore, that both of the high-modifications are hexagonal.

The exact symmetry classes of the two are not known.

[20] Article cited in XII, note [12].

[21] Rose, Gustav, *Über das Krystallisationssystem des Quarzes,* Physik. Abh. Kön. Akad. Wiss. Berlin, **1844**: 217-274, pls. 1-6.

[22] Groth, P., *Ueber Krystallform und Circularpolarisation und über den Zusammenhang beider beim Quarz und überjodsauren Natrium,* Monatsb. Kön. Pr. Akad. Berlin, **1869**: 140-148, 1 pl.

Experimental evidence on the symmetry of the tridymites

The true symmetry of low-tridymite was at first somewhat uncertain. Lasaulx[23] thought it triclinic, but Mallard[24] found that its optical characteristics indicate orthorhombic symmetry, and this view is supported by the observations of Fenner and others.

The external shape of the crystals yields no information on the symmetry of low-tridymite, because this shape is not natural but is impressed, being inherited from the high-modifications. The character of the twinning is of some help, but the main reliance is upon the optical properties.

No observations or measurements have been made on the crystal-forms or angles of upper high-tridymite at temperatures where it is stable; but since the crystals retain their external shape after inverting to low-tridymite, it is not difficult to decide, by measurements at room temperature, what is the general symmetry of the upper high-modification. Our knowledge of its symmetry rests almost entirely upon such measurements, made principally by the discoverer of the mineral, vom Rath.[25]

Experimental evidence on the symmetry relations of the tridymites

At the 117° inversion the faint birefringence of a basal section of low-tridymite suddenly disappears as the temperature rises. On cooling, the birefringence does not reappear until about 90° is reached, and is not fully reestablished until about 20° lower.[26]

At the 163° inversion no optical change can be detected, either on isotropic basal sections or on slightly birefringent tilted sections.

Fenner accordingly suggests that the relation between the upper high and the lower high modification may be that of holohedral hexagonal to hemihedral hexagonal symmetry. The argument is entirely by analogy with the two modifications of quartz.

Twinning in the tridymites

Low-tridymite

Low-tridymite is invariably twinned. Its twinning is of the type called *secondary*, that is, it has been produced subsequently to the original formation of the crystal. In the present case, this secondary cause is the inversion from high-modification to low-modification, all known tridymite having been formed at a temperature above the inversion temperature 117° and therefore having been subjected to the change in symmetry accompanying the inversion.

The individuals of the low-tridymite aggregate are always small, and

[23] Lasaulx, A. von, *Ueber das optische Verhalten und die Krystallform des Tridymites*, Zeitschr. Kryst. (1878) **2**: 253-274.

[24] Article cited in IV, note [18].

[25] Vom Rath, G., *Ueber die Krystallisation und Zwillingsbildungen des Tridymits*, Monatsb. Kön. Pr. Akad. Wiss. Berlin, **1874**: 165-179.

[26] Fenner, C. N., articles cited in IV.

the character of the twinning therefore difficult to recognize. Its interpretation depends in part upon what axes are assumed as the basis of the symmetry. From a study of the optical properties it appears that the twinning-plane is a face of an orthorhombic prism, the acute angle of the prism being about 60°.

Whatever the interpretation of the twinning, it is a fact that it is controlled to a certain extent by the symmetry of the high-modification. The hexagonal plate of the latter divides up more or less regularly into twinned areas, as indicated in Figure XII.13, although the subdivision is seldom so regular as in the Figure.

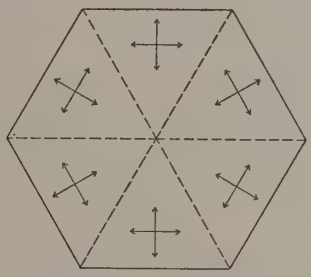


FIG. XII.13.—Relation of the orientation of low-tridymite to the outlines of the original crystal of high-tridymite.

Each area, in turn, consists of a number of orthorhombic individuals whose vertical axes coincide in direction with each other and with the vertical axis of the hexagonal crystal, but which are twinned after a 60° orthorhombic prism coinciding with the 60° hexagonal prism.

The high-tridymites

The principal mode of twinning of upper high-tridymite is that with a face of the pyramid $\{10\bar{1}6\}$ as twinning-plane. Repetition of this relation gives a triplet or *trilling*, a habit of growth which is so common in high-tridymite as to have given the mineral its name (see p. 42). Further repetition may lead to the formation of bundles of plates.

So far as we know this twinning persists without change in lower high-tridymite.

As already remarked, no observations or measurements have been made on the crystal-forms and angles of upper or lower high-tridymite at temperatures where they are stable. Our knowledge of twinning in these modifications, like our knowledge of their symmetry, therefore depends almost entirely upon observations at room temperature, made upon aggregates of low-tridymite which have inherited the external shape of upper high-tridymite. This evidence, however, is quite sufficient.

Historical note on the symmetry of tridymite

Vom Rath, discoverer of tridymite, assumed that the symmetry of low-tridymite is hexagonal, basing this conclusion on the obviously hexagonal external form of its crystals, both natural and artificial. Microscopic examination of the behavior in polarized light of available crystals, most of which were thin hexagonal plates, seemed to confirm the belief that tridymite is hexagonal and uniaxial.

Schulze, in 1869, examining the crystals which G. Rose had just succeeded in making artificially, announced that tridymite is uniaxial and optically positive. Lasaulx, Zirkel, and Rosenbusch seem to have agreed to this view without making a special study of the mineral. Hautefeuille (1878) stated that his artificial tridymite plates did not depolarize plane-parallel light passing through them perpendicularly.

About ten years after the discovery Lasaulx undertook to study the mineral more carefully, and then found to his surprise that it is not uniaxial but biaxial, and very intimately twinned. It soon appeared that the symmetry assumed by vom Rath and the others is a pseudo-symmetry, but the reason for this fact could not be cleared up until Merian and Mallard proved the existence of a high-low inversion (see p. 126).

The symmetry of cristobalite

The true symmetry-system of low-cristobalite is somewhat uncertain. The units in which it is ordinarily obtained are too small for accurate measurement, and it would be very difficult, if not impossible, to get larger crystals on which accurate measurements of angles and of optical properties might be made.

The symmetry is probably tetragonal but may be orthorhombic. Not enough is known to define more exactly its symmetry class.

High-cristobalite, as judged by its optical properties, and by its external shape or habit when produced at temperatures above the inversion-point, is of isometric symmetry. Its symmetry class is unknown.

Symmetry relation between high-cristobalite and low-cristobalite

High-cristobalite, on inverting to low-cristobalite, breaks up into an intimate mixture of very fine crystals of the low-modification, having three prevailing directions of orientation such that the basal planes of the tetragonal low-crystals are parallel to the three faces of the cube of the high-modification.

Twinning in cristobalite

Low-cristobalite, like low-tridymite, seems always to be twinned.

Small crystals of high-cristobalite usually do not break to pieces in the inversion to low-cristobalite, though each crystal becomes divided into por-

tions of varying orientation. The division is sometimes irregular, but more often the new crystal portions of low-cristobalite are secondarily twinned, with a sharp twinning plane at 45° or 90° to the original cubic axis of the high-cristobalite. This may be considered as twinning after a 45° pyramid parallel to an original octahedral edge.

High-cristobalite itself is frequently found twinned. The commonest type, both in artificial and in natural crystals, is "spinel twinning" or twinning with an octahedral face, (111), as twinning-plane.

EXPERIMENTAL EVIDENCE ON THE SYMMETRY OF CRISTOBALITE

The tetragonal symmetry of low-cristobalite, as well as the relation of the axes to those of high-cristobalite, are shown by the following observations by Mallard.[27] A plate cut parallel to an inherited octahedral face of the high-modification shows three systems of plates, mixed in great confusion. A considerable part of the section is not birefringent at all, probably because of superposition of several crystal units, but the plates which are birefringent show negative elongation with extinction parallel to the bisectors of the octahedral face.

The square section formed by cutting the octahedron perpendicular to an isometric axis again shows the three systems of plates, one of them nearly unirefringent in parallel light, the other two strongly birefringent with positive elongation and with their directions of extinction of similar sign crossed at right angles to one another and parallel to the diagonals of the square. In convergent light no trace of the optic axis is seen in the birefringent plates, but in the third set is seen the black cross of a negative optic axis showing that the substance is optically negative.

The only reason for suspecting that low-cristobalite is orthorhombic instead of tetragonal is the fact noted by Mallard that the black cross of the negative optic axis, seen in the almost unirefringent plates of a section cut perpendicular to an isometric axis, moves slightly on rotation of the section.

Holmquist[28] observed the fine-grained twinning in cristobalite crystals from silica brick. In sections having a square outline two optical orientations at 90° to each other were visible. Two neighboring lamellae show extinction at 45° to their principal dimensions, and hence all extinguish together when the crossed nicols are at 45° to the lamellae. At the position of maximum brightness, however, the mutual boundaries are still plainly visible because of the slight overlapping of the lamellae and the consequent neutralization of their birefringence at the boundaries.

In octahedral and other sections the mimetic structure was less distinct and the birefringence smaller.

These relations indicate that each pseudo-crystal consists of three mutually perpendicular interpenetrating sets of lamellae of a substance which is probably biaxial.

[27] Article cited in IV, note [18].
[28] Article cited in V, note [9].

Historical note

The history of our knowledge of the symmetry of cristobalite has been parallel to that of tridymite. Vom Rath called it isometric, basing his opinion on external form. Then Bauer [20] made thin sections of vom Rath's original specimens, one section parallel to an octahedral face and another at random orientation, and found that the crystals were not homogeneous in structure. The examination showed also that the optical properties were not in agreement with the external isometric form, because while portions of each section were isotropic other portions were birefringent. The structure was not, however, such as would be characteristic of a pseudomorph.

Again, as with tridymite, the explanation came with the discovery of high-low polymorphism in the mineral.

Axial ratios of the crystalline modifications of silica

The interfacial angles of a non-isometric crystalline substance are not completely determined by its symmetry. They depend not only upon symmetry but also upon the relative spacing of the atoms along the different axes of its fundamental geometrical form.

If the actual spacing of the atoms is unknown, as is the case with most substances, it is still possible to assume that certain commonly-occurring forms are geometrically the simplest possible forms, and on this arbitrary basis to calculate from the interfacial angles the *axial ratios*.

Quartz

For substances of trigonal or hexagonal symmetry, such as quartz, one ratio suffices. The three equatorial axes of an imaginary perfectly-formed geometrical solid of trigonal or hexagonal symmetry are equal in length, and are usually designated by the symbol a. The vertical axis, designated by c, may vary in length relatively to a. The axial ratio is the value of c/a sometimes called simply c, with a assumed equal to unity.

Determinations of the value of c for quartz with reference to $a = 1$ vary from 1.0994 to 1.1018. It is not certainly known whether the variation is real or represents only accidental and instrumental errors, but it appears probable from the data that smoky quartz has a slightly higher ratio than clear quartz.

The most probable value at room temperatures and at atmospheric pressure is 1.100 ± 0.001.

Millerian axial angle

Some authors prefer to describe trigonal crystalline substances, such as low-quartz, with the aid of *Millerian axes* in place of the hexagonal axes described at p. 184. Under this convention the edges between the

[20] Bauer, M., *Ueber Cristobalit vom Cerro S. Cristobal bei Pachuca (Mexico)*, Neues Jahrb. Min. etc. **1887**, I: 199-200.

ee lower faces of the rhombohedron (Fig. XII.4) are the directions of axes. These axes therefore make equal angles with one another. The ee axes are also of equal length. The conventional positive senses of axes are: x upward to front, y upward to right, z upward to left. The iable parameter in the fundamental dimensions of the substance is now *axial angle* α in place of the axial ratio c.

The axial angle of low-quartz, corresponding to the axial ratio $1.100 \pm$ 01, is readily calculated by trigonometry to be $93° 57' \mp 2'$.

The description of trigonal substances by means of Millerian axes kes a more logical system of crystallographic descriptions as a whole, it is less convenient, and also less adaptable to the comparison of optical l similar properties, than the use of the Bravais-Miller conventions de- ibed at p. 185 and used throughout this book. This is particularly true en trigonal low-quartz and hexagonal high-quartz are to be compared.

The experimental data on the axial ratio of low-quartz

The basic data for the determination of axial ratio consist of measurements interfacial angles between faces whose position is not determined by ometry alone. An interfacial angle is usually stated in terms of the angle ween the normals to the faces. The positions of these normals may also stated in terms of the latitude and longitude of the point where the normal uld intersect a sphere, the normal being referred to a principal axis and ne selected zero meridian. The latitude is known as the *polar angle*.

The following purely geometrical data may be found useful in comparing perimental results on low-quartz and judging of their precision and accuracy:

Basis of calculations: $c = 1.1000$

		Effect of a change of $+ 0.0001$ in c
gle of Millerian axes	93° 56.99′	−0.192′
lar angle of first-order rhombohedron r r z	51° 47.21′	+0.152′
ombohedral angle rr (angle between nor- nals to 2 faces of rhombohedron)	85° 45.44′	+0.223′
gle rz (between normals to faces of first- rder positive and negative rhombohedrons)	46° 15.89′	+0.102′
sal angle mr (angle between normals to hombohedron and prism faces $(10\bar{1}1)$ and $(10\bar{1}0)$)	38° 12.79′	−0.152′

Some original measurements on the axial ratio of low-quartz at room tem- rature are summarized in Table XII.3.

Tridymite

Because of the uncertainty regarding the true symmetry of low- dymite, its axial ratios are also uncertain.

Considering it as an orthorhombic mineral, with a c-axis perpendicular

TABLE XII.3.

SUMMARY OF ORIGINAL MEASUREMENTS ON THE AXIAL RATIO OF LOW-QUARTZ.

Author	Year	Source	Angle *rz*	*c*
Kupffer	1823	Gotthard	46° 15.87′	1.1000
Kupffer *	1823	Gotthard	46° 16.06′	1.1002
Dauber	1858	Marmarosch Herkimer Co., N. Y.	46° 16.08′	1.1002
Kokscharow	1878	Ural	46° 16.50′	1.1006
Gill	1893	N. Carolina	(46° 17.73′)	1.1018
		Riesengrund	46° 15.70′	1.0998
		Rosenlaui (Smoky)	46° 17.08′	1.1012
Wright	1913	Herkimer Co., N. Y.	46° 15.9′	1.1000

* Recalculated by Dauber, 1858.

to the usual hexagonal plate of the high-modifications, a *b*-axis perpendicular to the usual prism face, and an *a*-axis perpendicular to *b* and *c*, the axial ratios may be assumed to derive geometrically from the high-modifications and may be taken as $1 : \cot 30° : 1.6529$, that is, 0.5774 : 1 : 0.9544.

The axial ratios of the high-tridymites have never been determined at temperatures where these forms are stable. But since low-tridymite inherits the external shape of the high-tridymite from which it is derived, and does so without appreciable breaking up of the crystal, it is possible to obtain the approximate axial ratio by measurements at room temperature. The volume-dilatation which takes place at the inversion-points is known to be small, and it is therefore probable that the thermal deformation at the inversion-points is also small. The true axial ratios of the high-tridymites are therefore probably not very different from the value measured at room temperature on the pseudo-crystal.

The high-tridymites are hexagonal, and therefore each has a single axial ratio *c*. The value obtained by measurements at room temperature is 1.653, and the values for the high-modifications in their temperature-ranges of stability are probably not very different from this.

RELATIONS BETWEEN THE SYMMETRY OF THE MODIFICATIONS OF SILICA AND OTHER SYMMETRIES

There are some interesting relations between the geometry of the forms of silica, as expressed in their symmetries and axial ratios, and the general geometry of points arranged in space according to other symmetries. Such relations are naturally of interest as a guide to the structure of silica.

Quartz

The common rhombohedron of low-quartz is not very far removed from a cube, as may be seen from the fact that the angles between its edges are each 93° 57′, as compared with 90° each for the cube.

The interesting fact is that the departure is so nearly 1/9 of the axial o for a cube. A cube, mounted on one corner so that its body diagonal vertical, is a special case of the rhombohedron. Its indices on a hexnal basis are $\{1,0,\bar{1},\frac{1}{3}\sqrt{6}\}$. If this be taken as the unit rhombodron in place of $\{10\bar{1}1\}$, then the common rhombohedron of quartz very near the imaginary rhombohedron $\{90\bar{9}8\}$. The latter has a true xagonal axial ratio of 1.0887 as compared with the measured value of 00 for quartz.

Correspondingly, the frequently-occurring quartz rhombohedron $0\bar{2}3\}$ becomes the imaginary form $\{30\bar{3}4\}$ in terms of a cube.

Beckenkamp [30] has pointed out that the principal face-zone axes of artz bring out this cubic relationship particularly well.

The high-tridymites

The high-tridymites, which are hexagonal, show a similar relationship cubic symmetry. The axial ratio is not known accurately, but can be tained approximately from measurements on low-tridymite, which inrits the external shape of the high-forms. As so measured the axial io is 1.653. The hexagonal axial ratio of the imaginary simple rhomhedral form $(30\bar{3}4)$, based on the cube as unit, is 1.633.

Vom Rath, the discoverer of tridymite, remarked on its close approach to bic symmetry as seen in the angle of 70° 36′ of its triple groupings, the gle of an octahedron being 70° 32′. Mallard [31] pointed out that this cubic aracter appears directly in the axial ratio 1.653, which is not far from

$$\sqrt{\frac{3}{2}} = 1.633.$$

Interrelations

Since both quartz and high-tridymite have these simple relationships isometric symmetry, they are of course related to one another. This is en in the fact that ⅔ of the axial ratio 1.653 of tridymite yields the mber 1.102, very nearly the axial ratio of low-quartz (1.100).

Beckenkamp has pointed out these relationships in several papers. ney can of course be stated in various other ways besides those given ove. For example, the inclination of the fundamental form of highdymite to the principal axis is 27° 39′. This is very near the inclinaon of the icositetrahedron $\{1, 1, 11\}$ or the triakisoctahedron $\{775\}$ a trigonal axis, namely, 27° 56′ 20″. (These two isometric forms ffer only in a rotation of 180° about a threefold axis.)

High-cristobalite is known to be of isometric symmetry. We therefore ve the series of polymorphous modifications: high-cristobalite, highdymite, high-quartz, low-quartz, all with isometric affiliations. Such a ries has been called *isotypic*.

[30] Beckenkamp, J., *Leitfaden der Kristallographie* (1919, Berlin), p. 72.
[31] Mallard, E., article cited in IV, note [18].

Chapter XIII. THE ULTIMATE STRUCTURE OF SILICA

Those properties of a substance which distinguish it from other sub stances depend primarily upon: (1) the character of the nuclei of its con stituent atoms—the personality, so to speak, of the atoms; (2) the arrange ment of planetary electrons about these atomic nuclei; (3) the arrange ment and orientation of the atoms (nuclei and electrons) in space.

The first two of these elemental qualities in silica have already bee elaborated, though briefly, in Chapters II and III. The discussion of th principal modifications of silica, in Chapters IV to VII, and of thei symmetry, in Chapter XII, has now paved the way for the consideratio of the third quality, the arrangement and orientation of the atoms in space

The structure of crystalline substances

Since all matter is made of atoms, and since crystallinity depends upo their orderly arrangement, it is of fundamental importance in the stud of crystalline structure to know in what ways such arrangements can b made and how they are interrelated. For this purpose we need a discus sion of the number and kinds of structures which can be built up b arranging sets of similar objects in patterns which are indefinitely ex tended. Such a discussion is rather to be considered a branch of geometr than of chemistry or physics, but it is a branch of geometry which seem likely to become a necessary part of the equipment of every physicist an chemist.

The geometry of crystalline structures is based upon the mathematica doctrine of *groups of movements,*—movements which leave sets of point unchanged in their pattern. The word "group" is used here in its math ematical sense, not its everyday meaning.[1]

There are 32 possible *point-groups* consistent with crystallographi symmetry. A "point-group" is a finite group of movements which hav the property of leaving the appearance of a finite figure to which they ar applicable unchanged, while at the same time leaving one point of th figure unmoved.

There are also 14 possible *translation-groups,* represented by the 1 regular *space-lattices.* A "regular space-lattice" consists of the sum tota of points of intersection of three non-parallel sets of planes, each set con sisting of a series of parallel planes separated by equal intervals.

The combination of these point-groups and space-lattices yields 23 infinite *space-groups;* these provide the frames for all of the possible way

[1] For a semi-popular exposition of its underlying philosophy see Keyser, C. J *Mathematical philosophy* (1922, New York), especially Chapter XII.

in which atoms and their attributes can be arranged in space in order to make a crystalline substance.[2]

The 32 point-groups correspond in symmetry to the 32 *symmetry-classes* of Chapter XII, and the 230 space-groups may therefore be distributed among these classes. These can in turn be assembled into 6 *syngonies,* or into the familiar 6 or 7 crystallographic systems.

This purely geometric doctrine tells us nothing about the symmetry or structure of the ultimate units or "repeats" which make up the structure. Crystallographic evidence rather indicates that the symmetry of a substance, as found from its outward forms and its properties, is seldom, if ever, controlled by the symmetry of the atoms or atom-groups which form the repeating units.[3] Hence it is entirely consistent with experimental fact to construct illustrations of the 230 space-groups in the form of models made up of straight sticks and wires to which are attached, at regular intervals, wax doll's hands such as are made by a doll-manufacturer,—every hand quite unsymmetrical but exactly like all its fellows, except that we have at our disposal equal numbers of rights and lefts.

Analysis of the structure by means of X-rays

As already noted (p. 182), the diffraction of X-rays by a crystalline fragment gives information as to the symmetry of arrangement of the diffracting centers, the atoms. But the service does not end there.

It is obviously desirable to carry the analysis of the structure of a substance beyond its symmetry-class, and to find first the space-group to which its atomic pattern belongs, and ultimately the structure of the possibly unsymmetrical conglomerate or doll-hand consisting of one atomic nucleus,—sometimes more than one,—accompanied by electron orbits and magnetic and electric fields, the whole serving as the structural unit of the crystal.

Until the application of X-rays to the problem, even the first step in this analysis was usually not possible, except through the introduction of hypotheses which were more or less speculative. Then Laue, Friedrich, and Knipping showed how facts about the distribution of atoms can be obtained by a study of the diffraction of X-rays in crystals. Data of this kind relating to silica will therefore be considered next.

Three principal methods of using the X-rays have evolved: (1) The "Laue photograph," consisting of a pattern of spots, obtained when a heterogeneous beam of X-rays is sent through a single crystal and is allowed

[2] The best full discussion of this subject in English is that given by H. Hilton: *Mathematical crystallography and the theory of groups of movements* (1903, Oxford) 262 pp. The complete theory was worked out independently about 1890 to 1894 by Fedorov in Russia, Schoenflies in Germany, and Barlow in England. The reference work in most general use is that of A. Schoenflies: *Theorie der Kristallstruktur* (1923, Berlin) 555 pp.

[3] Barlow, W., *On types of crystal symmetry in which no finite symmetrical crystal unit having the complete symmetry of the crystal is to be found,* Phil. Mag. (1923) (6) **46**: 638-640; Zeitschr. Krist. (1924) **60**: 133-135.

to impress a photographic plate; (2) the "Debye-Scherrer diagram," "Hull diagram," or "powder photograph," consisting of a set of curves (or a segment of the curves on a strip of photographic film), obtained when a homogeneous (monochromatic) beam of X-rays is sent through the substance after it has been powdered, so that the specimen consists of fine fragments oriented in all directions; (3) the "Bragg method," "reflection method," or "spectrograph method," consisting in the measurement of the angles of apparent reflection of a homogeneous beam from a given face of the crystal, usually by means of an ionization apparatus moving around a circle.

The "oscillation photograph," made by substituting a photographic film for the ionization chamber and rotating the crystal back and forth through a fixed angle; and the "rotation photograph," similarly arranged but with complete rotation of the crystal, may be considered modifications of method (3).

The Laue photograph gives indications of the symmetry, but does not permit of the actual determination of the pattern of atoms except in special cases. A combination of the Bragg method and the powder photograph permits the placing of the atoms with a high degree of certainty in the simpler types of symmetry, revealing not only the space-group of the pattern but also the relative distances apart of atomic centers in the places where those distances are not already known from the geometry of the pattern.[4]

Existing data on the positions of the atoms in the crystalline modifications of silica

The analysis of crystal structure by means of X-rays has not yet been developed to the point where the structure of a complex substance of hexagonal, trigonal, or orthorhombic symmetry can be determined with the completeness and certainty which are now possible for many isometric crystals. The modifications of silica (with the exception of high-cristobalite) are therefore not yet within the range of exact and unexceptionable determinations of structure, though there is no reason to doubt that they will be brought within that range during the next few years.

No atom-pattern can be considered reasonably certain until it is supported by X-ray diffraction data of such a variety that the angles and intensities of the diffracted rays can not possibly be explained by any other assumed pattern. We have attained this degree of certainty for several crystalline substances of isometric symmetry, but no atom-pattern of equal reliability has yet been put forward for any of the modifications of silica excepting high-cristobalite. It is still necessary to rely to a certain extent upon the procedure of theorizing about the shape and dimensions of the

[4] See Bragg, W. H., & Bragg, W. L., *X-rays and crystal structure* (1924, London) 322 pp. Wyckoff, R. W. G., *The structure of crystals* (Amer. Chem. Soc. Monograph, 1924, New York) 462 pp.

atom-triplet SiO_2 and about the way these triplets may be arranged in space, and to adopt the result which best fits all the known properties.

In the next two chapters there will be made an attempt to build up such hypothetical structures for several of the modifications of silica. We shall therefore be concerned here with the experimental data on atomic positions which must serve as the foundation for those hypotheses.

High-cristobalite will be considered first, because, being isometric, its symmetry is simpler than that of the other six crystalline modifications.

Cristobalite

The structure of high-cristobalite has been examined by Wyckoff[8] by means of powder photographs. The specimen employed was one used by White for heat-capacity measurements (p. 330), and had been made by devitrifying vitreous silica at 1560°. 9 photographs were taken, part at 290° and part at 430°, the average spacings at these two temperatures agreeing within 0.1 per cent. Photographs were also made in the same apparatus at room temperature, giving the spacings for 12 low-cristobalite lines, and these lines were in turn calibrated by means of 6 photographs from a finely powdered mixture of low-cristobalite and sodium chloride, the spectrum of the chloride being now a well-known standard. The measurements thus have a high precision, amounting to about half of the best attainable with such apparatus, the decrease in precision being due only to widening of the lines by a relatively thick specimen and by the broader slit which it is desirable to use at the high temperatures.

The symmetry-class of high-cristobalite is not known from any other line of evidence, hence the analysis must begin with the most general considerations. The primary result of the experiments is a series of 16 diffraction angles θ resulting from the measurement of 16 lines on each photographic film. Knowing the wave-length of the X-rays used, λ, we then have the fractional spacings, $\lambda/(2 \sin \theta)$, of the planes of atoms which yield these diffractions. This much information is readily obtained from the X-ray line spectrum of any crystal.

We must next know the crystallographic indices of each diffracting plane, and the order (first, second, third, etc.) of the apparent reflection which produces the line under examination. If the substance is isometric, the ratio between any two values of $\sin^2\theta$ is a ratio between integers. Indices must therefore be chosen such that the calculated values of $\sin^2\theta$ will agree with the observed within the limit of error. This is perhaps the least rigorous step in the deduction of the structure, although the choice is subject to fairly strict check in the comparison between the intensities of different orders reflected from a given plane.

With the indices and orders known, the edge of the "unit cube," a_0, the smallest dimension which repeats itself periodically in the structure, is readily calculated. The average for high-cristobalite comes out 0.7122 ± 0.0005 mμ.

The number (m) of molecules of the formula SiO_2—or rather *atom-triplets*, for we are not dealing with distinguishable molecular units as in a gas,—

[8] Wyckoff, R. W. G., *The crystal structure of the high-temperature form of cristobalite*, Amer. Journ. Sci. (1925) (5) **9**: 448-459; Zeitschr. Kristallogr. (1925) **62**: 189-200.

contained within a cube of the given dimensions can be calculated if the density is known. Taking the value given in Table XX.1 for 430°, namely 2.211; and for the mass of a hydrogen atom, 1.663×10^{-24} gram:

$$m = \frac{(0.7122 \times 10^{-7})^3 \times 2.211}{\frac{60.06}{1.008} \times 1.663 \times 10^{-24}} = 8.06$$

Any other value for m than 8 would give a density impossibly far removed from the facts. The geometrically repeating unit cube therefore contains 8 atoms of silicon and 16 of oxygen.

The arrangement of these atoms in space is the next problem. All of the 36 possible isometric space-groups must be considered, but it turns out that

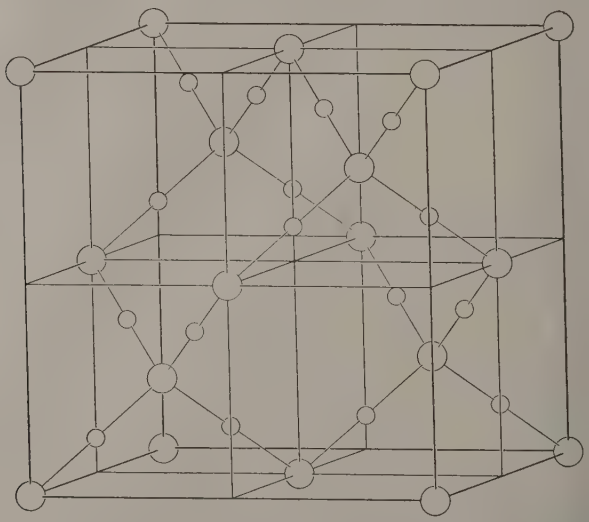


FIG. XIII.1.—Representation in space of the structure of high-cristobalite a determined by Wyckoff. Large spheres are silicon centers, small spheres are oxyge centers.

the choice can be narrowed down fairly quickly. The presence or absence o certain reflections forms the first criterion for eliminating some of the possi bilities. The first-order reflections from high-cristobalite are found to hav odd indices only, and this fact eliminates all structures developed from body centered space groups, also further reducing the remaining possible arrange ments to two. These two are both special cases derivable from any one o the three space-groups T_h^4, O^4, or O_h^7. In both of them the 8 silicon atoms a all equivalent to one another and the 16 oxygen atoms are likewise equivalen there are no sub-groups of 2, 4, 6, or 8.

Choice between these two is finally made by noting that they would yie

two different distributions of intensity among the lines, one of which is found n agreement with the data while the other is not. The first of the two is then he structure sought for.

The structure may be described by giving the coordinates in space, x, y, z, for the position of each atom. For the silicon, the arrangement is hat classified [6] by Wyckoff as (8f), while for the oxygen it is (16b):

$$\text{Si(8f)}: 000;\tfrac{11}{22}0;\tfrac{1}{2}0\tfrac{1}{2};0\tfrac{11}{22};\tfrac{11\bar{1}}{444};\tfrac{133}{444};\tfrac{313}{444};\tfrac{331}{444}.$$

$$\text{O(16b)}: \tfrac{111}{888};\tfrac{551}{888};\tfrac{515}{888};\tfrac{155}{888};\tfrac{177}{888};\tfrac{537}{888};\tfrac{573}{888};\tfrac{133}{888};$$

$$\tfrac{717}{888};\tfrac{357}{888};\tfrac{313}{888};\tfrac{753}{888};\tfrac{771}{888};\tfrac{331}{888};\tfrac{375}{888};\tfrac{735}{888}.$$

The coordinates given above are fractional parts of the unit distance a_0, neasured from a common origin.

The structure is represented in Figure XIII.1. Picture a cube with a ilicon atom at each of its eight corners and in the middle of each of its ix faces. Divide the cube by means of bisecting planes into eight smaller ubes, and place single silicon atoms at the centers of one-half of the small ubes, taken alternately. Then each silicon atom in the structure as a vhole is equidistant from four other silicons. Next place an oxygen atom alf way between any silicon atom and each of its four neighbors. The tructure is now complete.

The arrangement of the silicon atoms in this structure is the same as is in crystalline silicon, and the same as the carbon atoms in diamond. The type of structure of high-cristobalite differs from that of any crystal-ne substance yet examined.

The only respect in which the structure is not entirely satisfactory is n its failure to account completely for the relative intensities of the indi-idual lines of the X-ray photograph. The usual assumption upon which alculations of intensity are based is that the scattering power of an atom r ion for X-rays is proportional to the number of its planetary electrons see III). This relation is known not to be exact, but it gives approxi-nate agreement. Yet when the scattering powers of Si and O are taken n the proportion of their atomic numbers, 14 to 8, the agreement is decid-lly poorer than can be accounted for by any departure of the law from xactness, the calculated intensity being usually *less* than that observed. n the other hand, if the ratio of scattering power of silicon to oxygen is ken as 5 to 1 in place of 14 to 8, the calculated intensity comes out *reater* than the observed for 17 out of 18 lines examined. This suggests at the scattering power of silicon is greater per electron than that of xygen, instead of being the same, which was the initial assumption. This atter will be referred to again in Chapter XV.

[6] Wyckoff, R. W. G., *Analytical expression of the results of the theory of space oups*, Carnegie Inst. Publ. 318 (1922), pp. 104, 105, 144.

Data on the structure of quartz

The two modifications of quartz are closely related in symmetry and their X-ray patterns look very much alike. They may therefore be discussed together, so far as the experimental data are concerned. While the structure of neither of the two modifications can be said to have been determined with finality, the structure of high-quartz about to be described is highly probable. The structure of low-quartz involves hypotheses, and will be treated in detail in the next chapter, only its general features being presented here.

The principal X-ray data on quartz have been supplied by W. H.

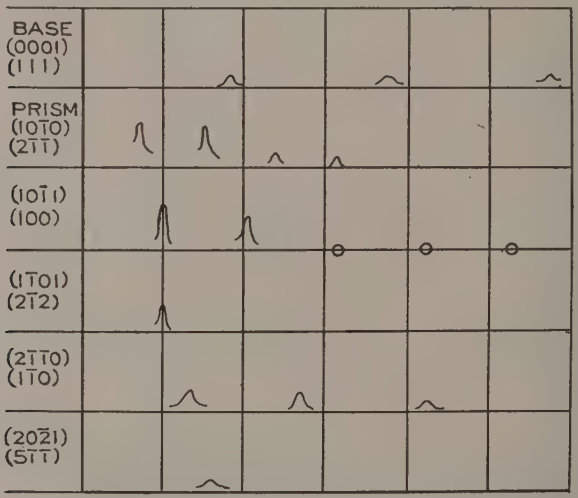


Fig. XIII.2.—Angles and intensities of the apparent reflection of X-rays from atomic planes in quartz. After Bragg.

Bragg, Wyckoff, and Gibbs. In addition we have photographs or measurements by Rinne, Haga & Jaeger, Mauguin, Hadding, and McKeehan.

The quartz lattices

The general foundation of the structure of quartz, as now generally accepted, was laid by Bragg.[1] He measured the angles of apparent reflec-

[1] Bragg, W. H., *The X-ray spectra given by crystals of sulphur and quartz*, Proc. Roy. Soc. London (1914) A **89**: 575-580. See also Bragg, W. H., & Bragg, W. L., *X-rays and crystal structure, first ed.* (1915, London, 229 pp., 4 pls.) pp. 160-167. The so-called second and third editions of this book seem to be identical with the first.

tion of X-rays from 8 different planes in a quartz crystal, using the radiation from a palladium target. The positions and intensities of the diffracted beams were measured by means of the ionizing effect of the rays in an ionization chamber, in a Bragg X-ray spectrometer. The results are shown in Figure XIII.2.

The spacings of like planes of atoms deduced from the data of Figure XIII.2 by means of the formula already used for cristobalite (p. 210)

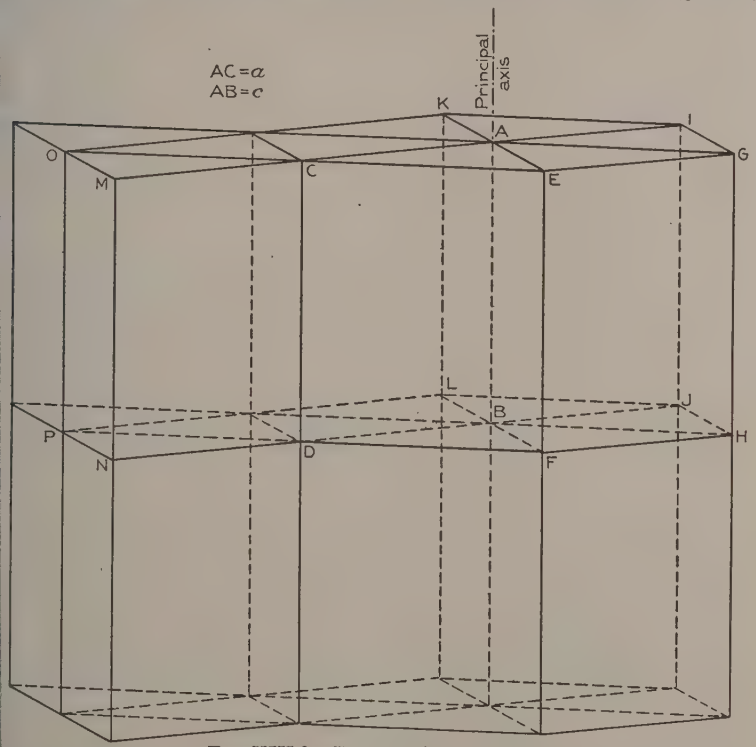


FIG. XIII.3.—Hexagonal space-lattice.

ndicate that the unit of structure repeated in its space-lattice contains 3 atom-triplets of the formula SiO_2, and also that the lattice is hexagonal (Γ_h). Bragg therefore interpreted the data by means of a structure based on a threefold hexagonal lattice, namely, three interpenetrating hexagonal lattices, derived from each other by equal translations parallel to the principal axis, together with rotations of 120° about that axis.

The hexagonal lattice Γ_h is made by the intersections of two vertical sets of planes making angles of 60° with each other, and one horizontal set per-

pendicular to the first two. The arrangement of points in the single lattice is illustrated by Figure XIII.3. The vertical planes form equilateral prisms with cross-sections such as ACEG, and the triangles in the figure are therefore all equilateral, that is, the distances AC, AE, AG, BD, BF, and so on, are all equal in length. AB is the interval between the horizontal planes of the lattice and differs from AC, etc., being in this case 1.100 times the length AC, to correspond with the most probable value of the axial ratio as derived from measurements of the angles of quartz crystals (see p. 202). It must be understood that this picture does not represent the shape of anything material; it merely tries to indicate how the points of the hexagonal lattice are arranged

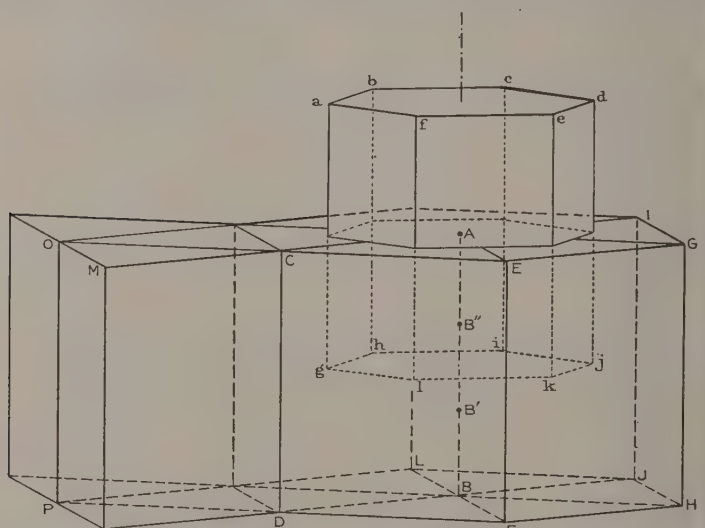


Fig. XIII.4.—Imaginary hexagonal cell which represents the share of completely occupied space belonging to one point of the hexagonal lattice.

in space. The figure is shown with a fish-tail in order to help in visualizing the arrangement. The actual lattice is supposed to be extended indefinitely in all directions.

According to the present interpretation, there are three SiO_2 atom-triplets to each unit of structure, and each hexagonal lattice locates the positions of one-third of the triplets.

To visualize this, let us imagine all the space in which the hexagonal lattice of Figure XIII.3 is supposed to exist to be divided up into equal portions, with a point of the lattice at the center of each portion. The portion belonging to the point A is shown in Figure XIII.4 as the hexagonal prism abcdefghijkl, whose volume is $\frac{1}{2}a^2c\sqrt{3}$, or twice the volume of one of the triangular prisms such as AGEBHF. A similar hex-

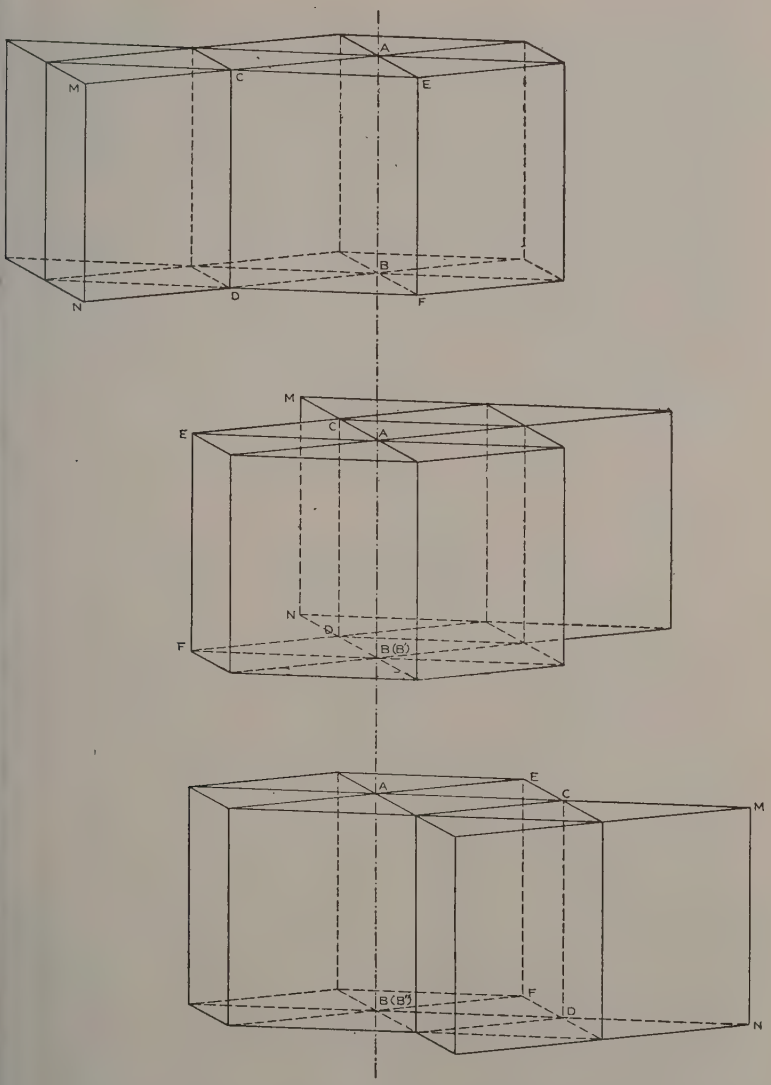


FIG. XIII.5.—Two 120-degree rotations of the hexagonal lattice preparatory to their intermeshing to form a three-fold lattice.

agonal prism may be imagined to surround every other point of the lattice (such as B, C, D, etc.) and together they completely fill the space.

Now plant an atom-triplet (SiO_2) somewhere in the hexagonal prismatic cell abcdefghijkl. The shape of the triplet and its exact position in the cell need not concern us at present. Further, have a triplet correspondingly placed and oriented in every other such imaginary cell. Then make two other independent hexagonal lattices exactly like the first one, each containing SiO_2 triplets in the same positions and orientations as the first.

Turn the second lattice 120° (one-third the way around) about the principal axis and intermesh it with the first one so that the point B′ of the second (corresponding to B in the first) comes on the line AB at one-third of the distance from B up to A. Turn the third lattice 240° (two-thirds of the way around) about the same axis in the same direction and intermesh it with the other two so that its point B″ comes at two-

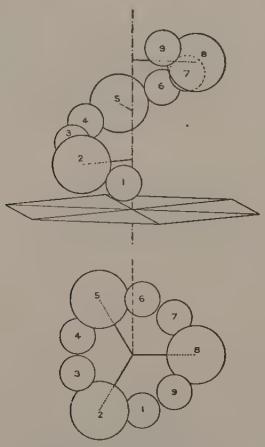


FIG. XIII.6.—Relation of silicon and oxygen atoms to the axis of threefold symmetry in quartz.

thirds of the distance from B to A. Figure XIII.5 shows parts of the three lattices after their rotation but before they have been intermeshed.

Evidently two independent structures of the kind just described are possible, the one clockwise, the other counter-clockwise in its direction of rotation. The rotation by which Figure XIII.5 was constructed was clockwise or right-handed, to an observer looking down upon it from above, and its motion was vertically upward; that is, the structure has the properties of a left-handed screw.[8]

[8] The description of screw motions is sometimes ambiguous or confusing because it is not realized that *three* specifications are necessary: (1) the orientation of the

The structure so obtained does not yet possess the necessary symmetry. Its space-group is C_3^2 (or C_3^3, if the rotation had been the other way). These groups are trigonal-pyramidal, and have a threefold axis only, while the symmetry of low-quartz is that of one of the groups D_3, which have, in addition to the threefold axis, three equatorial twofold axes. The SiO_2 atom-triplet, therefore, may not be placed at random in the imaginary cell, but must be placed on a twofold axis of the lattice in such a way that this axis is also a binary axis of the triplet.

Now the hexagonal lattice itself has 6 twofold equatorial axes. We therefore have a choice between two locations for the triplet, namely,

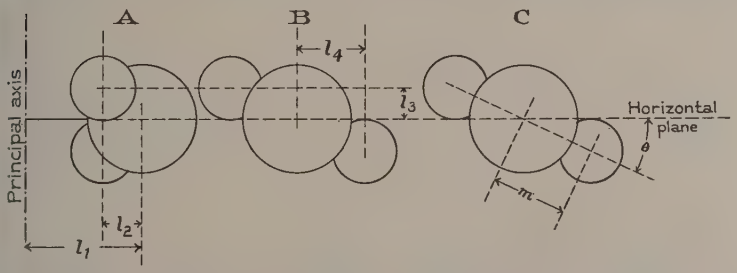


FIG. XIII.7.—Diagram to show the existence of four unknown parameters in the structure of low-quartz.

(a) : on a line joining the more distant pairs of points, such as AO; or (b) : on a line joining two neighboring points, such as AC. The rotation and intermeshing may now be performed as before. Choice (a) yields space-group D_3^3 (or D_3^5, if rotated the other way), while choice (b) yields D_3^4 (or D_3^6). Sohncke distinguishes these two by the names "composite 3-point screw system" and "alternating 3-point screw system," respectively (*zusammengesetztes* and *abwechselndes Dreipunktschraubensystem*).

In either case the set of three triplets, taken out by itself, will have a structure something like that illustrated in Figure XIII.6. The vertical line is the threefold axis, while perpendicular thereto are three twofold axes bearing the SiO_2 triplets, spaced at equal intervals along the vertical axis, and turned each 120 degrees from its predecessor. Figure XIII.6 has been derived by clockwise rotation, as seen from above, and upward translation.

There are four unknowns left undetermined, namely, the distance (l in Figure XIII.7) of the silicon atom from the threefold axis and the three parameters, such as l_2, l_3, and l_4, which are necessary to locate the oxygen pair with reference to the silicon atom.

translatory motion (vertical, north-south, etc.), (2) the sense of the translatory motion (upward, inward, northward, etc.), and (3) the sense of the rotation (clockwise, counter-clockwise).

Agreement of reflections with the general structure

If it be assumed simply that the lattice is hexagonal, and that the unit cell contains 3 SiO_2 atom-triplets, the angle of the first-order reflections of the X-rays can be calculated. Table XIII.1 gives a comparison of the calculated angles with those actually measured by Bragg.

The agreement is seen to be good in every case except that of the plane perpendicular to the axis. In this case the calculated angle is just *one-third* of that observed. The intermeshing of three hexagonal lattices with a vertical displacement of $c/3$ for each, as already described, accounts for this angle, while it leaves the other first-order angles unchanged.

TABLE XIII.1.

CALCULATED AND OBSERVED ANGLES OF APPARENT REFLECTION OF X-RAYS FROM FACES OF QUARTZ (BRAGG).

Plane	Index	Glancing angle	
		Observed	Calculated
First-order hexagonal prism	$(10\bar{1}0)$	3.9°	3.9°
Primary first-order positive and negative rhombohedrons	$(10\bar{1}1)$ } $(1\bar{1}01)$ }	4.93	4.95
Left second-order trigonal prism	$(2\bar{1}\bar{1}0)$	6.60	6.75
Left second-order trigonal bipyramid	$(\bar{1}2\bar{1}1)$	9.2	9.1
A first-order positive rhombohedron	$(20\bar{2}1)$	8.4	8.3
A first-order positive rhombohedron	$(10\bar{1}2)$	7.25	7.3
A first-order positive rhombohedron	$(10\bar{1}3)$	10.15	9.5
Base	(0001)	9.25	3.1

Wyckoff's data—Wyckoff's Laue photographs,[9] made with the rays at a small angle to the principal axis, give additional confirmation. Calculations could be made from several hundred reflections, and all of the possible cells of simple constitution, including that just described, were considered. A cell containing 4 triplets instead of 3 is geometrically possible, but is eliminated by the presence of several first-order reflections which such a cell would not have been able to produce.

McKeehan's data—McKeehan[10] has recently made X-ray powder photographs of low-quartz, from which he concluded, in agreement with Bragg and Wyckoff, that the lattice is hexagonal (Γ_h), and that the structure is helicoidal in character.

McKeehan attempted to carry the analysis further and to determine the four unknown parameters which fix the positions of the silicon and oxygen atoms (see p. 217). This can only be done with the aid of hypotheses which are open to some doubt. Hence the further consideration of McKeehan's structure as well as of the other hypothetical deductions that can be drawn from existing data on low-quartz, will be postponed to Chapter XIV.

[9] WYCKOFF, R. W. G., Zeitschr. Kristallogr. (1926) **63**: pp. 512, 513.

[10] MCKEEHAN, L. W., *The crystal structure of quartz*, Phys. Rev. (1923) (2) **21**: 503-508.

Structure of high-quartz

Leaving low-quartz at the stage of progress just outlined, we need to transfer attention to high-quartz in order to keep from wandering too far away from the easily demonstrable facts. High-quartz is the simpler of the two modifications in symmetry, hence there is a chance to obtain a unique solution of its structure. The necessary data have been provided independently by Wyckoff and by Gibbs.

Wyckoff [11] made powder photographs and reflection (Bragg) photographs from quartz above 573°, going as high as 750°, and also Laue photographs both above and below 573°. All of the patterns above 573° show perfect hexagonal symmetry. Since high-quartz is known to belong to the hexagonal

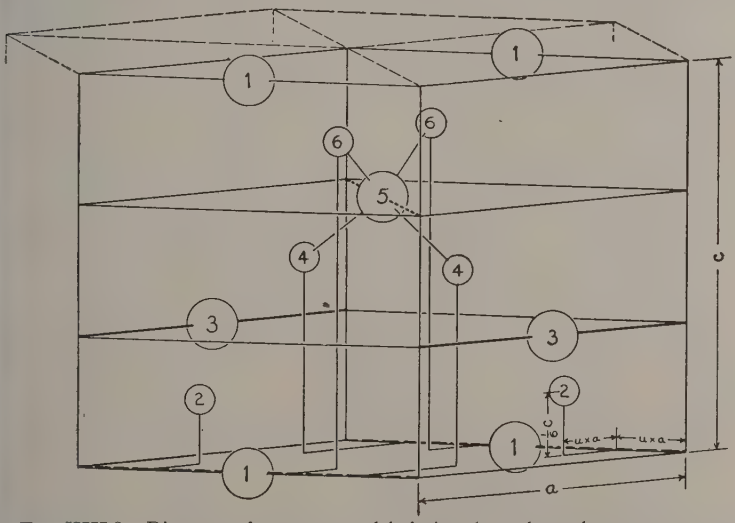


Fig. XIII.8.—Diagram of a space model designed to show the arrangement of silicon and oxygen centers in the unit cell of high-quartz. Large spheres are silicon centers, small spheres are oxygen centers. The heaviest lines (full, dashed, and dotted), and the numbers, correspond with similar lines and numbers in Figure XIII.9, part A.

trapezohedral class with respect to various other properties (see p. 189) its space-group is almost certainly of the symmetry of D_6 (see Table XII.1).

The strong similarity of the Laue photographs above and below 573° indicates that the unit cells of the two modifications are analogous. The hexagonal symmetry of high-quartz eliminates the possibility of a rhombohedral lattice, which might be permissible for low-quartz. A calculation similar to those for

[11] Wyckoff, R. W. G., *The crystal structure of the high temperature* (β-) *modification of quartz*, Amer. Journ. Sci. (1926) (5) **11**: 101-112. Zeitschr. Krist. (1926) **63**: 507-537. Prelim. publ. in Science (1925) **62**: 496-497.

cristobalite and for low-quartz then shows that 3 atom-triplets make the repeating unit, just as in low-quartz. A geometrically possible unit containing 4 triplets is eliminated by the same criteria of reflections as held good for low-quartz (see p. 218).

The next question is that of the space-group. There are 6 groups having the symmetry of D_6, of which only 3 need to be considered, namely, D_6^3; D_6^4; and D_6^5, which is the enantiomorphous twin of D_6^4. The first of the three is eliminated by the absence, both from spectrometer reflections and from powder photographs, of the first, second, fourth, fifth, etc., orders, leaving only the third, sixth, ninth, etc. This fact is consistent with D_6^4 and D_6^5 but not with D_6^3.

The actual positions of the nine atoms are next to be determined. D_6^4 and D_6^5 differ only in rightness or leftness, and so may be considered together, since both types of quartz are known. Under either group, there are 4 possible arrangements for silicon and 10 for oxygen, yielding in combination 8 possible structures. At this point it becomes necessary to appeal to relative intensities of the diffracted rays, but the differences upon which dependence is placed are large differences, such that the patterns are qualitatively distinguishable without actual measurements of intensity.

The eight structures mentioned have this in common, that each contains one undetermined parameter, u. It will be recalled that in low-quartz there were four such unknowns. In high-quartz the other three have been eliminated by the considerations discussed in the preceding paragraphs. It is necessary, therefore, in comparing the possible structures, to make estimates of the intensities from a whole series of assumed values of u. One fortunate result of this kind of a comparison is that an approximate value of u is obtained at the same time that the correct structure is discovered.

Four of the eight structures are quickly eliminated by weak third- and sixth-order reflections from the basal plane. Calculations for 20 lines for each of the remaining four structures were made on the assumption that the scattering powers of silicon and oxygen are proportional to their atomic numbers, 14 and 8, respectively.

Qualitative agreement in the intensities finally decides the choice in favor of the following structure under D_6^4:

Si:	$\frac{111}{223}$	$0\frac{1}{2}0$	$\frac{1}{2}0\frac{2}{3}$
O:	$u(-u)\frac{5}{6}$	$(-2u)(-u)\frac{1}{2}$	$u(2u)\frac{1}{6}$
	$(-u)u\frac{5}{6}$	$(2u)u\frac{1}{2}$	$(-u)(-2u)\frac{1}{6}$

with a corresponding structure under D_6^5:

Si:	$\frac{112}{223}$	$0\frac{1}{2}0$	$\frac{1}{2}0\frac{1}{3}$
O:	$u(-u)\frac{1}{6}$	$(-2u)(-u)\frac{1}{2}$	$u(2u)\frac{5}{6}$
	$(-u)u\frac{1}{6}$	$(2u)u\frac{1}{2}$	$(-u)(-2u)\frac{5}{6}$

The most probable value of u is 0.197 ± 0.004.

A few discrepancies in intensities still remain, but all of them are on planes with complicated indices. Their existence need not throw doubt on the structure, however, for similar discrepancies are still outstanding with even the best known of crystalline structures,—with calcite, for example. Their explanation will probably be found when we know more about the laws of scattering by atoms and ions.

The unit cell of the hexagonal lattice is a right prism with equilateral rhombic cross-section and with angles of 60 and 120°. The cell for the

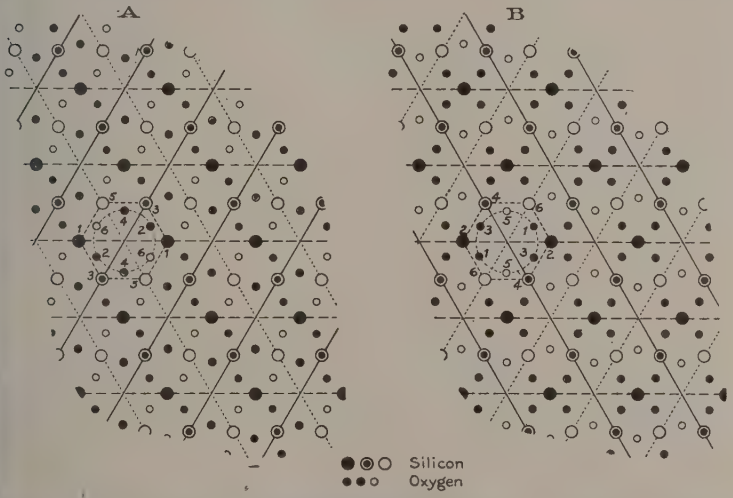


FIG. XIII.9.—Projection upon a horizontal plane of the structure of high-quartz. Part A represents the structure illustrated in Figure XIII.8, corresponding to space-group D_6^4. Part B is the enantiomorphous structure D_6^6.

first of the two structures of high-quartz just described is illustrated by Figure XIII.8.

The structure is illustrated in another manner in Figure XIII.9,A, which is a plan, or projection on a horizontal plane. The larger circles represent silicon atom-centers; the smaller circles, oxygen centers. At one part of the diagram, atoms in successive horizontal planes, from the bottom upward, are numbered 1 to 6. Number 7 would be directly above number 1. In this and other plans of the same type in this book the mnemonic rule is followed that the atoms nearest the bottom are the blackest. The outline of the figure is made irregular so that the eye will not be guided, and possibly misled, by the outward form of the drawing.

Part A of Figure XIII.9 represents the structure corresponding to space-group D_6^4. The enantiomorphous structure D_6^5 is represented in

part B. It will be seen that the two differ only in the direction of rotation of the helix. To emphasize the purely diagrammatic character of these projections the lowest layer of atoms in A is represented as consisting of silicon atoms, while the lowest layer in B is of oxygen atoms.

Bragg and Gibbs

The X-ray measurements of Gibbs,[12] supplemented and further interpreted by Bragg & Gibbs,[13] lead to the same structure for high-quartz as that just described. Gibbs made measurements of intensity on the first- and second-order reflections from three planes, at temperatures up to 800°. Bragg & Gibbs made single-crystal "rotation" photographs (see p. 208) at about 700° as well as at room temperature, and estimated the intensities from 24 planes.

Their result for the variable parameter of the structure of high-quartz is stated as a fraction of the distance across the hexagon formed by lines joining the projections of six silicon atoms as in Figure XIII.9. The oxygen centers lie within this hexagon, not more than one-eighth of the distance inward, and not less than one-sixteenth. One-twelfth is taken as the most probable value. It is readily calculated that this is equivalent to a value for Wyckoff's variable u (see p. 220) of 0.208. Wyckoff's value is 0.197.

Symmetry of the atomic pattern of quartz as indicated by Laue photographs

Although a Laue photograph, taken alone, does not permit of a final decision as to the arrangement of the atoms, it does give important information regarding the symmetry of that arrangement.

In interpreting such a photograph it must be remembered that the geometry of this photographic method may itself introduce a center of symmetry into the pattern.

High-quartz

The complete hexagonal symmetry shown in the Laue photographs made by Wyckoff and by Gibbs has already been remarked upon. Rinne [14] has published tracings of Laue photographs of both modifications, showing the difference in symmetry.

Low-quartz

Several investigators have published photographs, or descriptions and projections of photographs, taken by the Laue procedure on low-quartz. These show, for the most part, symmetry elements in accord with the

[12] Gibbs, R. E., *The variation with temperature of the intensity of reflection of X-rays from quartz and its bearing on the crystal structure,* Proc. Roy. Soc. London (1925) A **107**: 561-570.

[13] Bragg, W., & Gibbs, R. E., *The structure of α and β quartz,* Proc. Roy. Soc. Lond. (1925) A **109**: 405-427.

[14] Rinne, F., *Die Kristalle als Vorbilder,* etc. (1921, Berlin) p. 35. Rinne's α-quartz is high-quartz.

properties of the trigonal trapezohedral class in which low-quartz has always been placed by virtue of its interfacial angles and its physical properties.

Rinne[15] has published excellent reproductions of Laue photographs made by X-rays perpendicular to the photographic film and passing perpendicularly through plates of low-quartz parallel to the base, positive rhombohedron, hexagonal prism $\{10\bar{1}0\}$, and trigonal prism $\{11\bar{2}0\}$.

The basal plate (plate perpendicular to the vertical axis) shows the normal symmetry expressed in the threefold axis of the class, and the 3 apparent vertical planes of symmetry, bisecting the angles between the equatorial or horizontal axes, which planes are introduced by the Laue photograph itself.

The positive rhombohedron and first-order hexagonal prism photographs both contain one of these same fictitious planes.

The trigonal prism photograph contains only the twofold axis to which it is perpendicular.

A measurement of various facial angles from the Laue diagram of a basal plate of low-quartz was made by Rinne[16] with the results shown in Table XIII.2. Each measurement is the mean of the three made available by the threefold symmetry of the pattern of spots. The data given are the polar angles ρ of the various forms, that is, the angles between the principal axis and the normals to the faces.

The angles in the third column are calculated on the basis of an axial ratio of 1.0999, the basis of Goldschmidt's "Winkeltabellen" for quartz. The agreement is seen to be within 0.2° in nearly every instance.

The azimuthal angles can also be calculated. The azimuth Φ for the form $\{21\bar{3}1\}$ measures —71.0°; calculated value, —70.9°. The values of Φ for the other forms are determined by the symmetry alone and are therefore the same for all crystals of this symmetry.

TABLE XIII.2.

POLAR DISTANCES ρ OF VARIOUS POSSIBLE CRYSTAL PLANES IN LOW-QUARTZ, AS OBTAINED FROM A LAUE PHOTOGRAPH OF A BASAL PLATE AND BY CALCULATION (RINNE).

Form	ρ from photograph	ρ calculated	Difference
2$\bar{2}$1	68.8°	68.5°	+ 0.3°
3$\bar{3}$1	75.5	75.3	+ 0.2
4$\bar{4}$1	79.1	78.9	+ 0.2
0$\bar{2}$1	68.7	68.5	+ 0.2
0$\bar{3}$1	75.5	75.3	+ 0.2
0$\bar{4}$1	79.0	78.9	+ 0.1
1$\bar{2}$1	65.7	65.5	+ 0.2
1$\bar{3}$1	73.6	73.4	+ 0.2
2$\bar{4}$1	77.0	77.2	— 0.2

[15] RINNE, F., Ber. Kön. Sächs. Ges. Wiss. Leipzig, M.-P. Kl (1915) 67: p. 29, pls. 12-13.

[16] RINNE, F., Ber. Kön. Sächs. Ges. Wiss. Leipzig, M.-P. Kl (1916) 68: pp. 9-20, 23.

Haga and Jaeger[17] have made Laue photographs (with platinum- and tungsten-target tubes) of plates cut from a right-quartz crystal from St. Gothard. A plate parallel to the base, one parallel to the first-order hexagonal prism, and two parallel to the trigonal prism were used.

The basal and first-order prism plates, as well as one of the trigonal prism plates, show the normal symmetry already described.

The other trigonal prism plate, however, shows a vertical plane of symmetry in addition to the twofold axis. This plane is readily explained by twinning of the Brazil type (see p. 193) in this specimen. An apparent horizontal symmetry plane in both hexagonal and trigonal prisms, which the authors considered to be neither in accord with the generally accepted symmetry of quartz nor explainable by Brazil twinning, proved upon further examination to be non-existent.[18] The vertical dissymmetry in the later photographs is not, however, very marked. It is hardly more than would be introduced by a slight accidental tilting of the plate away from perpendicularity to the X-ray beam.

Other X-ray data on low-quartz

Mauguin[19] has recently studied Laue photographs of plates of quartz cut parallel to several different faces. The results are described but not reproduced. Plates parallel to the base and to the trigonal prism show the normal symmetry already described, while one parallel to a rhombohedral face again shows the fictitious vertical plane.

Of special interest is the absence of the plane $(2\bar{3}51)$ from all three of the foregoing as well as from a plate parallel to the positive rhombohedron; plane $(50\bar{5}2)$ is also missing from all of them except the rhombohedron.

It is also of interest to note that adjacent rhombohedral faces (positive and negative), which are known to develop differently and etch differently, differ in Laue pattern. The planes $(30\bar{3}1)$, $(23\bar{5}2)$, $(14\bar{5}1)$, and $(32\bar{5}4)$ are intense in a photograph of a plate parallel to the *positive* rhombohedron, while the corresponding conjugate planes in the *negative* rhombohedral plate are very faint. The planes $(2\bar{3}51)$ and $(50\bar{5}2)$ referred to above as missing from the positive rhombohedron and several other plates, are intense on the negative rhombohedron.

Gibbs[20] has made the most extended study yet published of intensities in the Laue pattern of low-quartz. He measured the relative intensities from 30 or more planes, with qualitative comparisons of many others. The results seem to agree completely with those of Mauguin, just quoted, in so far as they apply to the same planes.

Data of this kind form the necessary basis for conclusions as to the most probable structure for low-quartz, although as yet they are insufficient to

[17] Haga, H., & Jaeger, F. M., Kon. Akad. Wet. Amsterdam, Versl. Wis-en Nat Afd. (1915) **24**: 443-459; Proc. Sect. Sci. (1915) **18**: 542-558.

[18] Haga, H., & Jaeger, F. M., Kon. Akad. Wet. Amsterdam, Versl. Wis- en Nat Afd. (1916) **24**: 1612-1617; Proc. Sect. Sci. (1916) **18**: 1552-1556.

[19] Mauguin, C., *Utilisation possible des diagrammes de diffraction des rayons X pour la détermination complète de la structure de quartz,* Compt. rend. Acad. Paris (1921) **173**: 719-721.

[20] Gibbs, R. E., *Structure of α quartz,* Proc. Roy. Soc. Lond. (1926) A **110**: 443-455.

establish that structure with certainty. They will be considered again in the next chapter.

X-ray powder photographs have frequently been used in the identification of inorganic substances by comparing the spacing and intensity of the lines in the photograph from a known substance with the spacings and intensities in the unknowns. Hadding[21] has employed them in this way to identify quartz in various materials, and has tabulated the average spacings and intensities of the lines produced by the rays from an iron target on a film of 50 mm radius.

Dimensions of the low-quartz lattice

Whatever be the details as to the arrangement of the silicon and oxygen atoms, we know with fair certainty the average volume which is assignable to each and every SiO_2 atom-triplet in low-quartz. The mass of the hydrogen atom, 1.663×10^{-24} gram, is now a well-established constant of nature, and we also know that the average mass of the SiO_2 atom-triplets is $\frac{60.06}{1.008}$ times that of the hydrogen atom, within the limits of error of the atomic weights of silicon and hydrogen as compared with oxygen. The average volume per SiO_2 atom-triplet in low-quartz at 20° is, then, the mass of the triplet divided by the density of low-quartz, or $\frac{60.06 \times 1.663}{1.008 \times 2.649} \times 10^{-24}\text{cc} = 37.40 \times 10^{-24}\text{cc}$.

Knowing the volume assignable to each SiO_2 we can calculate the dimensions of its imaginary cell if the shape of the cell is known. If low-quartz has an hexagonal structure such as those suggested by Bragg, by Wyckoff, and by McKeehan, or a rhombohedral structure such as that proposed at first by Beckenkamp, there are three atom-triplets in each imaginary hexagonal cell abcdefghijkl (Figure XIII.4). The ratio of height to diameter of the cell is given by the axial ratio of low-quartz, which is 1.100. Therefore the shorter diameter of the cell, which is equal to the dimension AC in Figure XIII.4 or the parameter a of the lattice, is 0.000 000 4903 mm or 0.4903 mμ; and the height AB (or c) of the cell, which would be the distance between two silicon atoms in corresponding vertical positions in the helix,—the first and the fourth silicons, for instance,—is 0.5393 mμ. This dimension is about a thousandth of the wave-length of green light.

It should be noted that these results are independent of any measurements on diffracted X-rays. They depend solely upon the assignment of a certain kind of pattern to the structure, upon the accuracy of the density of quartz at 20°, and upon the accuracy of the mass of a hydrogen atom. The dimensions can be independently measured, however, in terms of the angles of diffraction of the X-rays.

An independent measurement of this kind on the horizontal distance

[21] Hadding, A., Zeitschr. Krist. (1923) **58**: 108-112.

between vertical planes of like atoms parallel to a face of the hexagonal prism has been made by Siegbahn & Dolejsek.[22] This is apparently the most exact direct determination that we have of a dimension of the lattice of low-quartz. The distance D between planes is found to be 0.424 66 mμ at 18° C. The distance a, which is equal geometrically to $2D/\sqrt{3}$, is therefore 0.490 35 mμ.

The ultimate constant on which this value is based is the "grating constant" of calcite, that is, the distance between planes of like atoms parallel to the rhombohedral cleavage plane of calcite. This figure is 0.302 904 mμ as determined by Siegbahn in 1919. The wave-lengths of certain characteristic X-rays from metals,—wave-lengths which are as reproducible as the more familiar optical spectrum lines,—were measured by reflection from calcite, and these same rays were then reflected from a prism face of quartz in order to determine its grating constant. The determination is in effect a comparison between the densities of calcite and quartz by way of precise linear and angular measurements. The data are summarized in Table XIII.3.

Table XIII.3.

Measurements of the Atomic Grating Constant of Quartz for Planes Parallel to a Face of the Hexagonal Prism. Siegbahn & Dolejsek, 1922.

Radiation	t	Angle of reflection	Average at 18°	Wave-length λ in mμ	D mμ
		° ′ ″	° ′ ″		
$K\alpha_1$ of Cu.....	16.0	10 25 40.0	10 25 39.7	0.153 730	0.424 69
	17.0	10 25 41.5			
	16.0	10 25 39.5			
	16.0	10 25 40.9			
$K\alpha_1$ of Fe.....	16.0	13 08 55.8	13 08 56.1	0.193 230	0.424 71
	16.2	13 08 57.8			
	17.0	13 09 00.6			
	16.2	13 08 54.6			
$K\alpha_1$ of Cr.....	16.0	15 36 32.0	15 36 59.7	0.208 484	0.424 59
	16.0	15 36 34.2			
	15.0	15 36 30.8			
	16.0	15 36 28.8			
					0.424 66

High-quartz

The distances between similar atoms in high-quartz can also be calculated in the way just shown, if its unit cell contains three atom-triplets.

[22] Siegbahn, M., & Dolejsek, *Erhöhung der Messgenauigkeit innerhalb der Röntgenspektren. II,* Zeitschr. Physik (1922) **10**: 159-168.

Taking the density at 600° as 2.533 (Table XX.1) and the axial ratio as 1.0921 (Table XX.5), we find the following dimensions:

Volume of equilateral rhombic prism	117.36×10^{-24} cc
Side of base of prism, a	0.499 mμ
Height of prism, c	0.545 mμ

Tridymite

On tridymite we have no X-ray data from which definite conclusions as to the relative positions of the atoms can be drawn.

Hadding [23] states that "natural tridymite has a diagram which cannot be distinguished from that of quartz." The test must have been made on a quartz pseudomorph of tridymite, a mineral variety which is found occasionally, for tridymite has been shown by other investigators to have a distinct pattern of its own.

The fact that the fundamental atomic arrangements in quartz, tridymite, and cristobalite are essentially different is abundantly demonstrated by X-ray powder photographs, such as the following:

R. W. G. Wyckoff, Geophysical Laboratory (1923). Unpublished photographs of quartz, tridymite, and cristobalite, made for purposes of identification of the forms.

A. W. Hull [24] (1922). Photographs of quartz, tridymite, and cristobalite, all taken in the same apparatus and under the same conditions.

Kyropoulos [25] (1917). Photographs of quartz and cristobalite, taken with rays from a platinum target, through powders of grain-size ½ to 1 μ. Container, tubes of silk paper. Exposure, 3 hours. The cristobalite was made by melting water-glass with sodium phosphate.

Data on vitreous silica

The earlier X-ray photographs from vitreous silica indicated no systematic structure whatever, as was to have been expected for an amorphous glass. With longer exposures and greater care for experimental details it is possible, however, to obtain photographs showing diffuse bands. Similar bands are obtained from ordinary glass.[26] Diffuse patterns are likewise given by various liquids, under conditions which eliminate the effect of the container.

The explanation and interpretation of the genuine though diffuse patterns obtained from liquids and glasses is not yet clear. Ultimately, no doubt, they will supply us with information about the structure of these substances.

[23] Trans. English Ceram. Soc. (1925) **24**: p. 32.
[24] Quoted and published by WASHBURN & NAVIAS, J. Amer. Ceram. Soc. (1922) **5**: 565-585.
[25] Article cited in X, note [20].
[26] WYCKOFF, R. W. G., & MOREY, G. W., J. Soc. Glass Technol. (1925) **9** (Trans.): 265-267.

For the present we can only say that in homogeneous vitreous silica there are no large clusters of regularly oriented atoms, the word "large" being used to mean clusters having a diameter of several hundred atoms; for if there were many such clusters, we should get distinct lines in the X-ray photograph, instead of diffuse bands.

Mitter, in Bragg's laboratory, could find no X-ray evidence of crystallinity in a specimen of vitreous silica made by the Thermal Syndicate, and used by Ray for latent heat measurements.[27] A powder photograph of vitreous silica, made by A. W. Hull and published by Washburn and Navias,[28] shows only uniform blackening. Other observers, also, have failed to detect any evidence of orderly arrangement in the glass.

Kyropoulos[29] made powder photographs of vitreous silica, powdered to a grain size of ½ to 1 μ, with X-rays from a platinum target. He reports that only the general blackening due to heterogeneous scattering could be observed. The same result was obtained with a rod of vitreous silica. Examination of his published photographs, however, shows that he obtained the same diffuse bands as have been observed by Wyckoff. If he had compared his photographs of vitreous silica with other photographs made under similar conditions but using liquids, he could hardly have failed to notice a difference in the patterns.

Deductions from the positions and intensities of such bands will have to be made with caution, however, because in any given case the bands may easily be nothing but artifacts, and not reproducible phenomena characteristic of the substance under investigation.

[27] Ray, R. C., Proc. Roy. Soc. London (1922) A, **101**: p. 515.
[28] Article just cited.
[29] Article cited in X, note [20].

Chapter XIV. THE HYPOTHETICAL STRUCTURE OF LOW-QUARTZ

In the preceding chapter were given structures for high-cristobalite and high-quartz which are fairly dependable, but the number of unknown parameters in low-quartz proved to be too large to permit of a final solution of its structure. We may now attempt, by the aid of various hypotheses, to select a structure for low-quartz which will fit the available data, although the result will be subject to change if the hypotheses turn out to be wrong.

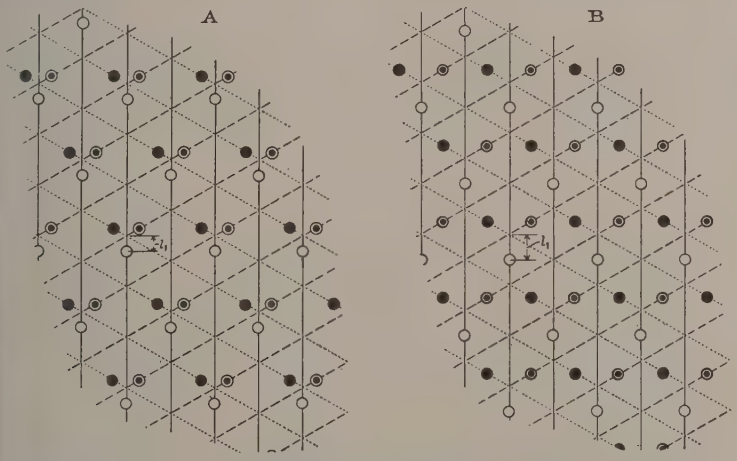


Fig. XIV.1.—Plan showing the range of values of l_1 (Figure XIII.7) in a "composite" hexagonal pattern.

Possible positions of silicon atoms

It will be profitable first to examine, as a purely geometric problem, the possible range of values for l_1, the distance of the center of the silicon atom from the principal axis (see Figure XIII.7).

If $l_1 = 0$, the pattern of the silicon atoms is a simple hexagonal prism lattice with a value of c just one-third of that assumed in Figure XIII.3. The assumption $l_1 = 0$ is equivalent to assuming that the silicon atom was on the principal axis of the cell abcdefghijkl in Figure XIII.4 when we placed the atom-triplet SiO_2 in the cell.

If l_1 is greater than zero, there are two cases to be considered (see p. 217):

(a) The twofold axes are taken perpendicular to the sides of the equilaterals, that is, in directions such as AO in Figure XIII.3; this yields space-group D_3^3 or D_3^5, Sohncke's "composite" structure.

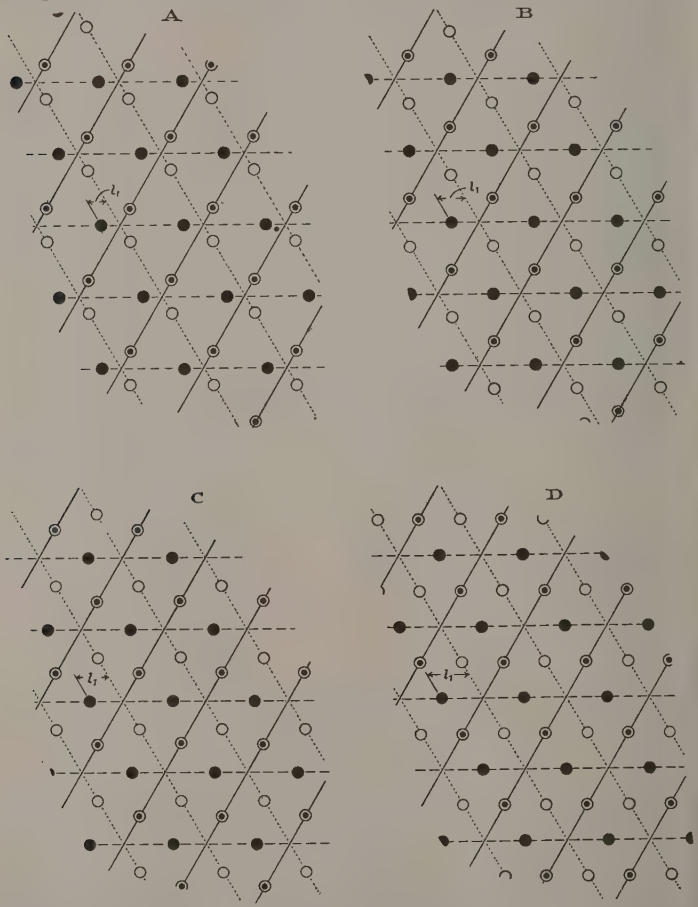


FIG. XIV.2.—Plan showing the range of values of l_1 (Figure XIII.7) in an "alternating" hexagonal pattern.

(b) The twofold axes are taken parallel to the sides of the equilaterals, that is, in directions such as AC in Figure XIII.3; this yields space-group D_3^4 or D_3^6, Sohncke's "alternating" structure.

Case (a). *"Composite" structure*

If l_1 is slightly greater than zero we have a structure such as that shown in plan in Figure XIV.1,A.

In this and the succeeding illustrations the solid black spots represent the lowest horizontal layer of silicon atoms, the circles with dotted centers represent the next layer above, and the open circles represent the top layer, the structure being then repeated indefinitely above and below these three. The structures shown in Figures XIV.1 and XIV.2 have right-handed or clockwise rotation upward, as viewed by an observer looking from above; in other words, they have the geometrical form of a left-handed screw. Those in XIV.1 belong to or are derived from space-group D_3^6; those in XIV.2, from space-group D_3^6.

The value $l_1 = \frac{1}{6}\sqrt{3}a$, that is, l_1 = one-third of the height of the equilateral, represents the limiting case, illustrated by Figure XIV.1,B. If l_1 is increased beyond this value, the same patterns are obtained as when l_1 is less than $\frac{1}{6}\sqrt{3}a$.

The value $l_1 = \frac{1}{3}\sqrt{3}a$ or two-thirds of the height of the equilateral, finally, is equivalent to $l_1 = 0$.

Case (b). *"Alternating" structure*

We pass next to the case (b), where l_1 is measured parallel to the sides of the triangle.

When l_1 is slightly greater than zero, the silicon atoms take the pattern illustrated in Figure XIV.2,A.

$l_1 = \frac{1}{3}a$ gives a special case (Figure XIV.2,B), in which the silicon atoms assume a rhombohedral pattern, and right-handedness or left-handedness disappears.

Figure XIV.2,C represents the structure when l_1 has been increased a little beyond $\frac{1}{3}a$.

Figure XIV.2,D shows the limiting case, in which $l_1 = \frac{1}{2}a$. If l_1 is increased beyond $\frac{1}{2}a$ a structure is obtained which is a duplicate of that represented in Figure XIV.2,A. When $l_1 = \frac{2}{3}a$, Figure XIV.2,B is duplicated. Finally, $l_1 = a$ is equivalent to $l_1 = 0$.

It will be noticed that $l_1 = \frac{1}{6}\sqrt{3}a$ in case (a) and $l_1 = \frac{1}{2}a$ in case (b) give the same patterns for the silicon atom-centers.

This completes the possible patterns for the silicon atoms. The two oxygen atoms may now be attached and the patterns considered further.

Symmetry of the triplet

A space-group of trigonal trapezohedral symmetry may have as many as 6 equivalent points. If it be granted that there are only 3 atom-triplets in the unit of structure of low-quartz, then the triplets themselves must have a binary axial symmetry with respect to any property of the triplet which can influence the symmetry of properties of the substance as a whole.

Shearer[1] has carried the argument further and stated the opinion that the binary symmetry of the triplet arises *only* from a twofold axis. This would mean that the atoms themselves would not have the perfect symmetry of spheres, else the triplet would have 2 symmetry planes. To avoid this, it would need an axis about which it could be turned 180° without any change in its appearance, but it should not be capable of reflection in a plane without such change.

This deduction seems hardly justified. The symmetry of properties of a substance, even the symmetry of arrangement of diffracting centers as revealed by X-rays, is not necessarily influenced by the shapes of the atoms, and a particular atom or a group of atoms may possess elements of symmetry which do not become apparent externally.

Positions of the oxygen atoms

We need assume, then, merely that the triplet has at least binary axial symmetry. The simplest representation of this in terms of the structure of the substance is the placing of the silicon atom-center on a binary axis, and two oxygen atom-centers at equal distances on either side of this axis on a line perpendicular thereto.

The 3 parameters necessary to fix the positions of the oxygen centers are thus left undetermined. They may be stated in terms of Cartesian coordinates l_2, l_3, and l_4, as was done in Figure XIII.7, A and B, or by means of the coordinates l_2, r and θ, as in Figure XIII.7, A and C.

Principles and hypotheses which may be used in elucidating the structure

It will be useful to state at this point some of the general lines of argument that can be applied to the problem of determining the four unknown parameters of low-quartz.

Angles

First comes the principle of diffraction itself, controlling the angle at which the rays come out from the crystal, either after passing entirely

[1] Shearer, G., *The relation between molecular and crystal symmetry as shown by X-ray crystal analysis,* Proc. Phys. Soc. London (1923) 35: 81-98, p. 91.

hrough it, or after penetrating to the depth of a few hundred atoms and hen being apparently reflected out from a face.

The glancing angle of reflection, θ, from any plane of atoms is determined by the formula: $\sin\theta = \frac{o\lambda}{2l}$, in which o is the order of the eflection (first, second, third, etc.), λ is the wave-length of the X-rays, nd l is the vertical distance between successive planes. There is no eason for questioning the exactness of this relation.

Intensities

The intensity of a ray, indicated by the blackness of its line or spot in he photographic negative, is the next criterion. The intensity depends ıpon the scattering power of the diffracting centers, the atoms. The usual ssumptions are:

(A) The intensity of reflection by any set of planes of atoms is inversely proportional to $\sin^2\theta$.

(B) The scattering power of an atom is proportional to the number of its non-nuclear electrons.

These two principles are known to be inexact, though not widely in rror. They are supplemented by two other purely empirical principles:

(C) The scattering power per electron of a heavier element is slightly greater than that of a lighter element, instead of being the same, as supposed in (B).

(D) The difference described in (C) becomes greater as the indices of the reflecting plane become more complex.

Under these principles the scattering power of an ionized atom differs rom that of a neutral atom, because it contains more or fewer electrons ıan the neutral atom. Accordingly, hypotheses as to the manner of comination of silicon and oxygen come into the calculation. The extreme ases (see pp. 36 and 37) are:

(E) The combination of silicon and oxygen produces no ionized atoms.

(F) The combination of silicon and oxygen is due to the transfer of electrons, leading to the formation of a quadruply charged positive silicon ion and two doubly charged negative oxygen ions.

Inter-atomic distances

The probable size of atoms or ions, meaning the distances between their enters when they are brought as close together as they can be brought, ıay also come into the argument. Without holding to any definite hypothses regarding the shapes of atoms, it is still legitimate to estimate a "radius of combination" for a given atom, which is its contribution to the xing of the distance between its center and that of its neighboring atoms.

Pure silicon has been shown by Debye & Scherrer [2] and by Hull [3] to have a tetrahedral cubic structure, of the type sometimes called "hexagonal close-packed" or "the diamond structure." Knowing this fact, we can find from the density and atomic weight of silicon that the diameter of a spherical silicon atom is 0.235 mμ, imagining simply for purposes of calculation that each atom is a sphere, and that the spheres are in contact. It is a permissible assumption that silicon atom-centers can not be brought much closer together in any compound than they are in the pure element. Hence:

(G) The minimum distance between silicon centers in quartz may be taken as 0.235 mμ.

Limits may also be set by the probable diameter of the radius of combination of an oxygen atom. An estimate of this quantity made some years ago [4] places it at approximately 0.065 mμ as deduced from the structures of ZnO and other oxides. Accordingly we may add as further tentative hypotheses:

(H) The nearest approach of two oxygen centers is 0.130 mμ.

(J) The nearest approach of an oxygen and a silicon center is 0.183 mμ.

While a set of values of atomic radii may be consistent within itself, a change in one of the radii necessitates changes in all the others. That some change is necessary in the values assumed above is shown by the facts that the silicon-oxygen distance in high-cristobalite, as calculated from Wyckoff's measurement and structure (see p. 209), is 0.154 mμ; and the distance calculated from the structure and dimensions of high-quartz is 0.161. A modification of hypothesis (J) is therefore needed:

(K) The nearest approach of an oxygen and a silicon center is 0.150 mμ.

Other arguments which are less direct than the foregoing may be drawn from various physical properties of quartz, and especially from its external morphology and its types of twinning. These may be considered in subsequent chapters in connection with the properties in question.

Numerical limits due to atomic sizes

Some fairly definite limits can be set at once on the basis of the principles and hypotheses just stated.

The value zero for l_1 (Figure XIII.7), which is equivalent to placing the silicons one above another along the principal axis, is seen at once to be very improbable, because the distance between planes of silicon

[2] Debye, P., & Scherrer, P., Physik. Zeitschr. (1916) 17: p. 282.
[3] Hull, A. W., Phys. Rev. (1917) (2) 10: p. 683.
[4] Bragg, W. L., Phil. Mag. (1920) (6) 40: p. 174. Later opinion makes the oxygen atom considerably larger, and the silicon atom correspondingly smaller.

toms in quartz is known to be only 0.180 mμ (see p. 225), which is much ess than the assumed diameter of the silicon atom, 0.235 mμ.

In the next place, the assumed minimum inter-atomic distance of .235 mμ and the known interplanar distance 0.180 mμ combine geo- netrically to set a minimum value on l_1, which is readily calculated to be .065 mμ.

The maximum value for l_1 if the structure is of "composite" type $(D_3^3$ and $D_3^5)$ is $\frac{1}{6}\sqrt{3}a$ or 0.142 mμ; if of the "alternating" type $(D_3^4$ nd $D_3^6)$ it is $\frac{1}{2}a$ or 0.245 mμ. These maxima are geometrical, and not ependent upon atomic radii.

Position of oxygen planes

The intensities of the reflections also furnish definite qualitative evi- ence as to the positions of the oxygen atoms. Bragg [5] found that the ntensities of the first, second, and third orders of reflection from the asal plane are as 38:40:24, and are all small compared with the reflec- ions from other planes. This shows that the oxygen atoms can not lie n the same horizontal planes as the silicons, else we should have a series f intensities which decrease rapidly, and the first-order intensity would lso be greater than it is found to be.

This fact rules out of consideration the structure proposed by Mc- Keehan.

McKeehan's interpretation

McKeehan [6] made the first attempt to carry the analysis of low-quartz be- ond the stage described in Chapter XIII. He did this empirically, by trying arious possible and reasonable combinations of dimensions, calculating the pproximate intensities of the first six reflected rays and comparing these alculated values with the observed intensities. About thirty different arrange- ents were tried, including Huggins' hypothetical structure (see p. 241), and he arrangement which best fitted the observed intensities was adopted. The etailed data have not been published.

Although they are not explicitly stated in the article, the hypotheses in- olved in McKeehan's calculations are those indicated above as (A), (B), F) and (H). The combination of hypotheses (B) and (F) makes the cattering powers of the silicon and oxygen centers the same, which seems ery doubtful in view of Wyckoff's experiments on cristobalite and high- uartz. (See p. 211.)

Bragg & Gibbs' interpretations

Within the quantitative limits already discussed there is still a con- derable range of choice of position for silicon and oxygen atoms.

[5] Bragg, W. H., & Bragg, W. L., *X-rays and crystal structure*, 4th edition (1924, ondon) p. 264.

[6] Article cited in XIII, note [20].

Having found that the oxygens can not be in the same horizontal planes with the silicons (θ or l_3 in Figure XIII.7 not equal to zero) we may next inquire whether they may be equidistant from successive silicon planes ($l_3 = \frac{1}{6}c$). Gibbs' and Mauguin's comparisons of intensity between conjugate rhombohedral planes, such as $20\bar{2}3$ versus $02\bar{2}3$, show that such an arrangement is not probable, else the intensities of the two sets would not differ so greatly.

The relations between intensities of reflections from basal planes, already mentioned (p. 235), can now be further used. They are closely accounted for [7] if the oxygen centers are assumed to lie in planes spaced about 0.063 mμ above and below the horizontal silicon planes. This value is near one-third of the spacing between silicon planes, or $c/9$. One of the

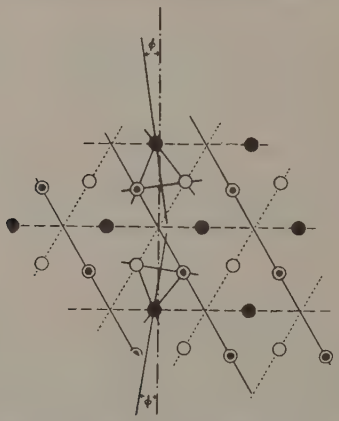


FIG. XIV.3.—The difference between parts C and D of Figure XIV.2 partially stated in terms of an angle of rotation, ϕ.

four unknown parameters is thus determined, namely, $l_4 = 0.063$ mμ at room temperature (Figure XIII.7).

The most recent and most exhaustive correlation of intensities and structures to determine the other three parameters in low-quartz is that of Gibbs.[8] Basing his tentative structures on that of high-quartz, he finds that the most probable alteration in structure required to produce low-quartz is (1) a movement of the silicon centers of about 0.030 mμ away from their high-positions; with (2) a movement of the oxygen centers out of their original common plane, midway between two silicon planes, into two distinct planes as described above; and (3) a distortion

[7] GIBBS, p. 562 of article cited in XIII, note [13].
[8] GIBBS, R. E., *Structure of α quartz*, Proc. Roy. Soc. Lond. (1926) A, **110** 443-455.

of the arrangement of oxygen centers about a silicon center, an arrangement which was originally nearly tetrahedral.

Gibbs' structure involves principles (A) and (B) above, with trials also of hypothesis (F) in combination with the so-called intensity factors calculated by Hartree, which modify the scattering power according to the structure.

It involves also an assumption which we may call hypothesis (L):

> (L) The relation between a given silicon and its four neighboring oxygens is the same for all the oxygens—in other words, no molecular groupings are visible in the structure.

This assumption has the effect of fixing a second one of the four parameters.

The change from high-quartz, described above in general terms, has the effect of rotating all the projected triangles of silicon atoms in the horizontal plane of Figure XIII.9 a few degrees away from their original parallelism, as may be seen by a glance at Figure XIV.2, Part C, as compared with D. A partial description of the change can accordingly be given in terms of this rotation, as is illustrated in Figure XIV.3. This variable constitutes a third parameter. The rotations tried ranged from 4 to 16.°

Hypothesis (L) is equivalent to saying that the oxygen center shall lie in a plane which bisects, and is perpendicular to, the line joining two silicon centers. The first parameter which was fixed (see p. 236) placed it in the horizontal plane which lies at a distance 0.063 mμ from a silicon plane. Hence it must lie on the intersection of these two planes, with linear variability only. Accordingly, the fourth and final parameter may be taken as the linear distance of the oxygen center from the line joining the silicon centers. Various values of this distance were tried, in combination with various values of the "rotation parameter" of the preceding paragraph. The combination which best fitted the observed intensities was a rotation of 8° with a linear distance of 0.044 mμ.

A plan of the structure thus determined is given[9] in Figure XIV.4.

Beckenkamp's interpretation

On morphological grounds Beckenkamp[10] prefers the arrangement shown in plan in Figure XIV.5. He accepts the placing of oxygen atoms in planes at a distance $c/9$ from a silicon plane, but leaves the silicon centers unmoved in their high-position, producing all the change from high- to low-quartz by movement of oxygen centers. These are placed on the diagonal of the vertical rectangle which constitutes a face of the hexagonal

[9] This and the other quartz structures described in Chapters XIII and XIV are represented in so many different ways in the original articles that I have reconstructed them all in a consistent style which should permit of easy comparison.

[10] BECKENKAMP, J., *Zur Entwickelung unserer Kenntnis von der Atomstruktur des trigonalen* (α) *und des hexagonalen* (β) *Quarzes,* Private publ. June, 1926, 8 pp.

prism at whose corners are silicon atoms of corresponding planes (the first and the fourth planes, for example). Their order of arrangement with respect to silicon centers is indicated by the numbering in Figure XIV.5.

Some earlier hypotheses

Several earlier hypotheses of the structure of low-quartz may profitably be considered at this point, to illustrate some of the possibilities that have been tried and found wanting.

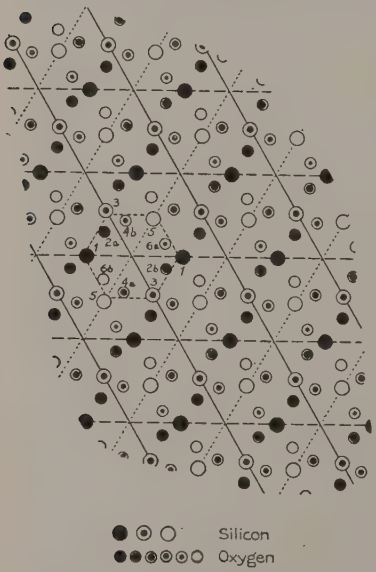


Fig. XIV.4.

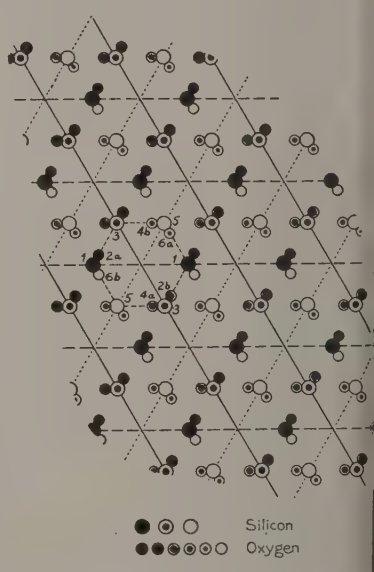


Fig. XIV.5.

Fig. XIV.4.—Plan of the structure of low-quartz according to Gibbs, redrawn for comparison with XIV.2, etc.

Fig. XIV.5.—Plan of the structure of low-quartz according to Beckenkamp, redrawn for comparison with XIV.4, etc.

Fresnel, Reusch, Briot, and other physicists and optical mineralogists early recognized the likelihood that some type of helical arrangement of structural units would be needed to explain the rotatory power of quartz and its enantiomorphous growth-forms.

Sohncke

Sohncke[11] after first adopting a composite structure (D_3^3 and D_2^5), selected an alternating structure (D_3^4 and D_2^6) as being much more probable in low-

[11] Sohncke, L., *Ueber Spaltungsflächen und natürliche Krystallflächen,* Zeitschr. Kryst. (1887) **13**: 214-235, p. 229.

quartz than the composite, because it fits in much better with the rhombohedral habit of quartz.

Bragg & Bragg

Probably because of this presumption in favor of D_3^4 and D_3^6, Bragg & Bragg [12] considered only this structure and not the case D_3^3 and D_3^5. They concluded that the arrangement of silicon atoms is that which has already been illustrated in Figure XIV.2,A, with a value of l_1 such that the lines joining a given silicon-center to the silicon above it and to the one below it make the tetrahedal angle, namely, 109° 28′. This would lead to the value $c/\sqrt{5}=$ 0.241 mμ for the distance between silicon centers, only a little larger than the value 0.235 found for pure crystalline silicon.

The silicon atoms were assumed to be bonded by sharing electrons (see II) and the vertical helical succession of silicon atoms would thus make a continuous helix whose axis would be parallel to the *c*-axis. Oxygen atoms form the connecting links between silicon atoms of neighboring helixes. Each silicon atom is connected in this manner to four other silicon atoms, two in the horizontal plane above and two in the plane below.

This arrangement of the atoms brings any horizontal plane of oxygen centers into a position half-way between planes of silicon centers. As a whole, it does not give as good agreement with the observed intensities as the structure adopted later by Bragg & Gibbs,[13] and it has therefore been abandoned.

Beckenkamp

Believing that Bragg's first strictly hexagonal structure would not satisfactorily explain the optical properties or the morphology of low-quartz, Beckenkamp [14] proposed a special adaptation of that structure, based upon a rhombohedral lattice for the silicon atoms. This is the special case B in Figure XIV.2, since the rhombohedral pattern may be considered as a three-fold triangular prismatic pattern derived by rotation and translation.

Thus far the structure is similar to those already described, but with the distance l_1 of the silicon atoms from the rotation-axis set at the special value $\frac{1}{3}\,a$, making the right-handed and left-handed rotations indistinguishable.

The quality of right or left-handedness must then depend upon the positions of the oxygen atoms in the structure. In right-low-quartz, Beckenkamp placed the oxygen atoms on the diagonals of the rectangles which constitute the faces of the hexagonal prism at whose corners are silicon atoms of corresponding planes (such as the first and fourth), and placed their centers at one-sixth the distance along the diagonal from the silicon center. This causes planes of oxygen atoms to lie half-way between planes of silicon atoms.

In a variant of this structure the oxygen centers are placed at one-ninth the distance along the diagonal instead of one-sixth. Two equidistant planes of oxygen atoms then lie between two silicon planes.

The first structure is illustrated in Figure XIV.6, which is a plan or hori-

[12] Bragg & Bragg, *X-rays and crystal structure,* 4th ed. (1924, London) pp. 260-265.

[13] p. 408 of article cited in XIII, note [13].

[14] Beckenkamp, J., *Über die Anordnung der Atome und die optische Drehung bei Quarz und bei Natriumchlorat,* Zeitschr. anorg. allg. Chem. (1920) **110**: 290-310.

zontal projection similar to the preceding Figures. In the numbered group, numbers 6*b* and 2*a*, 2*b* and 4*a*, and 4*b* and 6*a*, respectively, are the pairs of oxygens associated with silicon atoms which are numbered 1, 3, and 5. The series of 9 atoms (3 SiO_2 triplets) thus forms a helix rotating upward to the left. The same plan will serve for the variant structure described above, if the pairs of oxygen centers are thought of as brought $a/18$ closer to the silicon centers, and if the designations *a* and *b* in the numbering are considered to indicate different planes.

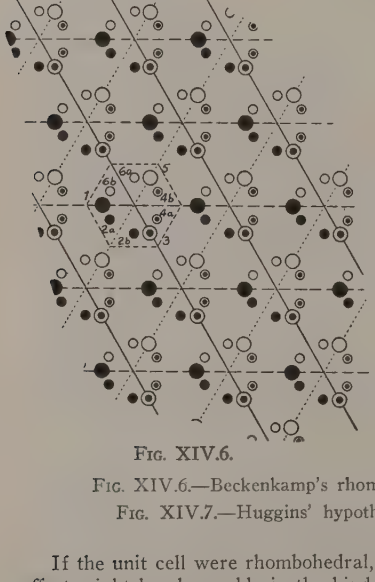


FIG. XIV.6.

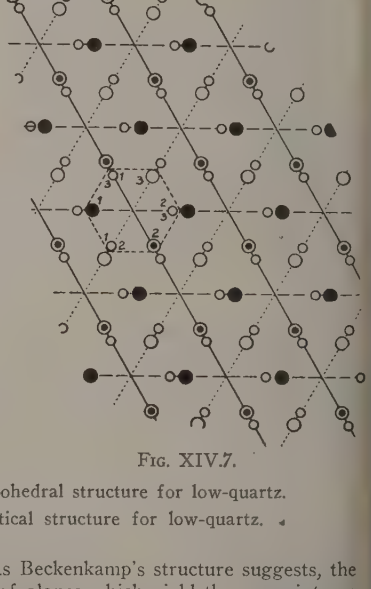


FIG. XIV.7.

FIG. XIV.6.—Beckenkamp's rhombohedral structure for low-quartz.

FIG. XIV.7.—Huggins' hypothetical structure for low-quartz.

If the unit cell were rhombohedral, as Beckenkamp's structure suggests, the effect might be observable in the kinds of planes which yield the more intense reflections.[15] If the preponderant planes in the photograph are such that all three of the quantities: $(2h+i+l)$, $(i-h+l)$, and $(-h-2i+l)$ are divisible by 3 (the Bravais-Miller indices being represented by *h, i, k, l*), then the presumption is strong that the lattice is rhombohedral. If there is no such preponderance, which is the case with quartz, the chances are against its being rhombohedral, although that possibility is not excluded.

Beckenkamp has now abandoned his rhombohedral hypothesis in favor of a structure based on the known structure of high-quartz (see p. 219), but has retained the feature that the right- or left-handedness depends only upon the positions of the oxygen centers, not upon the silicons, whose arrangement remains hexagonal, as in high-quartz.

[15] WYCKOFF, *Structure of crystals* (1924) p. 346.

Huggins

Huggins [16] has offered a hypothetical structure for quartz, consistent with a hexagonal lattice and based on the Lewis-Langmuir hypotheses of the construction of chemical compounds in general. Huggins' fundamental hypothesis falls under (E) above (see p. 233). It supposes that all the linkages between atoms in low-quartz are primary-valence linkages between silicon and oxygen, making the crystal a continuous edifice, and so classing it with those substances in which, as in sodium chloride, only atoms are recognizable within the structure, but no atom-groups or individual molecules. This has subsequently been found to be true of high-quartz.

It will not be necessary here to consider Huggins' hypotheses as to the bonding of silicon and oxygen, but only the resulting distribution of atoms in space. Two structures are described, one of which we may call "ideal," the other, "modified."

The proposed ideal arrangement in space is illustrated in Figure XIV.7 (plan). Its dimensions are fixed by the following assumptions: (1) Each atom-center is equidistant from the two or four atom-centers to which it is bonded; this makes the arrangement of oxygen centers about a silicon center tetrahedral; (2) The oxygen centers are on the twofold axes; (3) The oxygen centers are in the same horizontal planes as the silicon centers. The space-group is D_3^4 or D_3^6 (not D_3^3 and D_3^5 as stated by McKeehan). The arrangement of silicon centers is that of Figure XIV.2,C, and the distance between oxygen and silicon centers is 0.197 mμ.

In the "modified" structure the distance between oxygen and silicon centers is assumed to be 0.182 mμ (see hypothesis (J)) instead of the 0.197 mμ calculated above. Since one of the other assumptions must yield, a departure is permitted from the perfect tetrahedral arrangement. Some of the resulting dimensions have been calculated by McKeehan.[17] These structures are rejected by Bragg & Gibbs because of the strong evidence that oxygen and silicon are not coplanar (p. 235).

Ichikawa

Ichikawa [18] has published diagrams representing the hypothetical structure of quartz. He assumes as his unit a "crystal molecule" containing 6 atom-triplets of SiO_2, but does not show the axial distribution in his diagrams. There must obviously be some helical arrangement, because if his illustrations of right- and left-quartz represented patterns in a plane they would be in effect identical, being simply views of the same structure from opposite sides. The bonding force in the atom-triplet is conceived by Ichikawa as electrical, each SiO_2 consisting of a positive ion (Si) and a negative ion (O_2) (see hypothesis (F)). The bonding forces in the crystal are not specified.

[16] Huggins, M. L., *The crystal structure of quartz*, Physical Rev. (1922) (2) **19**: 353-368.
[17] Article cited in XIII, note [16].
[18] Ichikawa, S., Amer. J. Sci. (1915) **39**: p. 469.

General features of the hypotheses

Most of the theories of structure of silica agree in giving to the triplet SiO_2 a triangular plan. As McKeehan points out, this may have an effect on its state of aggregation at a given temperature. The analogous compound carbon dioxide takes the form of gaseous molecules of CO_2, each of which is symmetrical about an axis passing through all three atom-centers.[19] It may therefore be expected to have relatively weak stray fields outside the molecule, and hence the mutual intermolecular attractions which cause condensation to the liquid form are small. A similar high degree of molecular symmetry in silicane, SiH_4, gives to this compound, as to CO_2, the ability to become a gas at a relatively low temperature.

SiO_2, on the contrary, is much less symmetrical than CO_2 or SiH_4, and may be supposed to have correspondingly larger external fields which cause the triplets to associate to form a solid at temperatures where the other two substances are gases. See Figure III.8 for a diagrammatic picture of a possible type of distortion.

As to the reliability of the different structures proposed for low-quartz, among which those of Gibbs and of Beckenkamp seem to have the best claim to survival, much depends upon the weight given to the different kinds of evidence. The results obtained with the aid of a rigid geometrical analysis which takes account of all the possibilities permitted by the theory of space-groups,—a type of analysis applied by Wyckoff to many structures,—are certainly more satisfactory, especially to the physicist, than conclusions reached by less rigid methods having more of a chemical than a mathematical flavor. On the other hand, "certainty" in science is a relative term, and some weight must be allowed even to hypotheses which are only qualitative. The crudity of some of the chemist's early principles, such as Dulong & Petit's law, is pathetic, until we perceive what genuine progress those principles brought about in the science.

[19] Rankine, A. O., Proc. Roy. Soc. London (1921) A **98**: 369-374.

Chapter XV. A GENERAL THEORY OF THE STRUCTURE AND POLYMORPHISM OF SILICA

Need of a theory

Having reviewed the modifications of silica and their interrelations, and having considered briefly the facts concerning their symmetry and structure, we are in a position to see what can be done toward constructing a consistent theory, or set of hypotheses,[1] which shall not only tie together the facts already presented but also serve as a framework for the presentation of the many additional facts still to be considered.

Strictly speaking, Chapters XIV and XV are out of their logical order. If we but had at hand the information about structure which we know is experimentally obtainable, we could follow up Chapters II and III, on the composition and atomic constitution of silica, with Chapters XII and XIII, on the symmetry and ultimate structure of its modifications. It would then be possible to correlate that knowledge with the known interrelations of the crystalline and amorphous modifications of silica. This, in turn, would supply the basis for a fairly complete explanation, in atomic terms, of the physical and chemical properties still to be considered.

The actual order of progress, however, is likely to be just the reverse of this,—we shall have to theorize about the shape and dimensions of the atomic and molecular units in silica and tentatively adopt the result which best fits the facts, in order, so to speak, to fill in the gaps in Chapters XII, XIII, and XIV.

I shall attempt in this chapter first to sketch the necessary outlines of a consistent theory, or set of hypotheses, concerning the structure and polymorphism of silica. This presentation will be accompanied or followed by the principal facts and arguments which have led to the adoption of the hypotheses. It will then be shown how these hypotheses fit in with some of the facts already presented. In succeeding chapters the theory will be further applied here and there, for the explanation of other properties.

It need hardly be said that each hypothesis cannot, at the moment, claim any large likelihood of permanence, because new facts, especially facts concerning the arrangement of the atoms in space and the structure of individual atoms, are rapidly being obtained. Nevertheless, if we can find a set of hypotheses which satisfies the greater part of the large body of existing facts about silica, it may prove to be the permanent basis for a dependable theory which will need to be modified only in minor points.

[1] *Hypothesis:* "A tentative conjecture assigning provisionally a cause for known facts, to be used as a basis for their arrangement and classification . . ." The word *theory* is used here to mean a group of such hypotheses, all of which are consistent one with another.

Materials for a theory

One can nearly always find a few specimens of quartz about a research laboratory, and there never was a museum, however small, which did not have some specimens of "rock crystal". Here, I suspect, is the reason why we now have such a variety of physical data on crystalline quartz; everyone who invented a new apparatus or method found quartz a convenient standard substance on which to try out his invention.

Vitreous silica comes next in the order of abundance of available data, because of its scientific and its industrial interest. Not so many facts are at hand on the other crystalline forms of silica, but, all told, a good deal is known about their relations to one another, as will be evident from the variety of data contained in this book.

This body of facts furnishes particularly attractive material for the entertaining pastime of theorizing about the structure of substances, since the process of building up a successful combination of hypotheses is the more complex and absorbing, the greater the variety of data to be explained.

This is an indoor sport in which anyone may engage. The reader, if he wishes, may skip this chapter and the theoretical sections of later chapters, and then, after reading the rest of the book, he may develop hypotheses of his own. Now, assuming for the sake of the comparison that he and I have the same material to build on, and that my general knowledge of physico-chemical science and my capacity for turning it over in my mind are equal to his, it will probably be found that his final result resembles mine in many respects, but differs widely from it in others. His hypotheses may explain all the facts just as well as mine do. One of us will be nearer right than the other, and the decision will depend, not upon our skill in debate, but upon some experiment not yet tried or some measurement not yet made.

At the same time we must not lose sight of one essential quality of a genuine hypothesis. It must not explain the phenomena with too much facility. It is no real virtue in a theory of polymorphism, for instance, that it is capable of explaining not only all the existing data but also any imaginable facts of polymorphism which remain undiscovered. A theory which is capable of explaining all imaginable data in its field is, conversely, incapable of predicting any one experimental fact to the exclusion of any other; or, in the pragmatic philosophy, it is not a theory at all, but a form of words. It has happened more than once in the history of science that two formulas which sounded very different, but whose corollaries were experimentally indistinguishable, have led to needlessly long and bitter polemics. Hence it will be well to devote our closest scrutiny to the deductions that follow from a given hypothesis, rather than to the plausibility and general attractiveness of the formulation itself.

Chapter III has described the constitution of the atoms of silicon and oxygen, and the ways in which they may combine to form the com-

pound SiO_2. The next problem is: what manner of association of the atoms or atom-groups causes the formation of liquid silica, glassy silica, and the various crystalline modifications?

At the very beginning of this inquiry it is important to know whether the atoms are associated in definite triplets of the formula SiO_2 or whether they are associated in some other manner.

The individuality of the SiO_2 atom-triplet

Every chemist believes that there are certain groups of atoms, particularly groups containing carbon, which retain an individuality in the gaseous, liquid, and crystalline states, whether the group be itself a pure substance, or a constituent part of a relatively complex compound. There is much evidence that this is true of the silica atom-triplet, SiO_2—I use "atom-triplet" instead of "molecule," since the word "molecule" has many connotations in which we are not now interested. This individuality of SiO_2 is recognized in our common groupings of chemical facts. In the textbooks of chemistry the silicates are recognized as a proper subject for unified treatment, while the sulfates or chlorides are classified according to their metallic constituents. Under atmospheric conditions the silicates are nearly all transparent crystalline solids, insoluble in water and the usual solvents. They melt above a red heat to form viscous liquids of low volatility. Most of them are easily converted into glasses, which are strikingly alike in many of their properties.

In a paper summarizing the phase-rule diagrams which represent the relations of composition and temperature in a number of two-component and three-component silicate systems, and commenting on some of their properties, I have emphasized the evidence furnished by those data in favor of the assumption that SiO_2 acts as a unit in the silicates.[2] Perhaps it is a group of the formula SiO_3 or SiO_4 instead of SiO_2, but there are many facts that point to the existence of some constitutional unit common to them all.

Let us assume, as a basis of argument, that the common unit is the SiO_2 atom-triplet itself, retaining a recognizable individuality in the silicates. We are justified, then, in extending the same conception to pure silica and may adopt as our first working hypothesis:

(A) *Silica exists as an individual triplet in all of its states of aggregation,—gaseous, liquid, vitreous, and crystalline.*

At once a weak place appears in the argument. If the above statement is true of the crystalline forms, it sets off silica as being markedly different from such strongly polar compounds as sodium chloride, for it is now clear from X-ray analysis that a crystal of NaCl is a structure built up of Na and Cl atoms, or rather ions, and is a structure within which no

[2] Sosman, R. B., *The common refractory oxides*, J. Ind. Eng. Chem. (1916) **8**: 985-990; Trans. Faraday Soc. (1917) **12**: 254-263; Year Book Carnegie Inst. Washington (1919) **18**: p. 155.

definite groupings of atoms are recognizable. Now recent determinations of the structures of high-cristobalite and high-quartz (see XIII) reveal a similar state of affairs. Each of these substances is seen as a continuous edifice of silicon and oxygen atoms, within which we can no more recognize definite triplets of the formula SiO_2 than we can recognize definite groupings of bricks in a plain brick wall.

To be sure, silica is not quite in the same case as sodium chloride, for the existence of ions (atoms which have gained or lost electrons) in the structure can not be asserted so confidently for silica as it can be for the salt. Calculations of lattice energy, compressibility, and other properties of diatomic salts on the basis of a structure of ions have been very successful, but no such success has attended similar calculations for triatomic compounds such as silica. Nevertheless, silica in the modifications high-quartz and high-cristobalite appears as a structure of atoms, not of molecules.

On the other hand, the X-rays do not see everything in a crystal. They reveal the average positions of diffracting centers in silica, but each such center consists of a nucleus which may have anything from eight to eighteen electrons circulating around it. Those electron-paths still remain concealed from us, and they can easily be conceived to be arranged in such a way as to give a recognizable existence to the atom-groups and molecules in which the chemist has always rested his faith.

Constitution of crystalline silica

Silica in its crystalline and vitreous modifications is an elastic solid over a wide range of temperature. This means that not only are the atoms associated in triplets but these triplets are in turn held together in a larger unit. To express it in other words, some "force" prevents the free movement of each triplet as a whole and holds it in a fixed position in the solid.

The nature of this force is not entirely clear. In some crystalline compounds, we may suppose, the process of forming the compound is one and the same with the process of forming the crystal, that is, the compound does not exist as molecules at all, even in the liquid or gaseous state. Some of the complex silicates, such as diopside ($CaSiO_3.MgSiO_3$), may be of this kind. Next would come those compounds which do exist as molecules in the gaseous and perhaps the liquid state, but which completely revise their mode of combination in the crystalline state so that the molecule either vanishes, as it seems to do in NaCl, or becomes an atom-group, as in Al_2O_3. Finally, at the other extreme are substances whose solid state may result entirely from the residual electric or magnetic fields of permanent stable molecules which are recognizable as such in all states.

As our second hypothesis, we shall assume that silica belongs in the intermediate class.

(B) *The solid state in silica is the result of a sharing or a transfer of electrons between neighboring atom-triplets.*

Our ultimate problem, then, is to find the pattern according to which the silicon and oxygen atoms are arranged in space, and to find some manner of either sharing or transferring electrons which will account simultaneously for the following results: (1) the formation of an SiO_2 triplet, (2) the building up of such triplets into solid substances of several different forms, and (3) the change undergone by each principal form at its high-low inversion.

Our most direct information as to the arrangement of the atoms comes from X-ray diffraction. The available data for silica have been presented in Chapter XIII, with some partly hypothetical extensions in Chapter XIV. The further development of the theory must, then, be based on the phenomena of polymorphism and the physical properties of the forms.

The polymorphism of silica

The most suggestive fact about the polymorphism of silica is its division into two strongly contrasted types. These have already been described fully in Chapters IV and VII, and only a brief restatement need be made here.

There is, first, the "sluggish" type of inversion which occurs among the three forms: quartz, tridymite, and cristobalite. All three exist at atmospheric temperature and pressure, although only one, quartz, can be stable under those conditions. Nevertheless the other two are very persistent and are not difficult to obtain. The principal feature of the inversions from one of these forms to another is their slowness, several hours usually being required for complete transformation, and at certain temperatures and in certain directions the presence of a solution or melt in contact with the silica is necessary before the change will occur at all.

The second type of inversion in silica is the "high-low" type, occurring between the high-temperature and low-temperature modifications of quartz, tridymite, and cristobalite. These inversions occur promptly the moment the proper temperature is reached, although it should be noted that this temperature may be different according to whether the temperature is rising or falling; that is, they show a temperature-hysteresis. But, outside of this hysteresis range, the high-modification is never found at a lower temperature, nor is the low-modification found at a higher temperature. As pointed out by White,[3] the phenomena suggest some change which is common to all the three forms, yet is affected by the transformation from one form to another.

In looking about for hypotheses to explain these two contrasted groups of facts we find, first of all, that hypotheses as to the cause of polymorphism have generally lumped together all its manifestations and have tried to

[3] White, W. P., Amer. J. Sci. (1919) (4) **47**: p. 31.

explain them by a single cause. The actual phenomena, however, show wide variations, which may well be traced to different causes.

The hypotheses which have been advanced to account for polymorphism may be roughly grouped as (1) molecular, (2) structural, (3) atomic.

The molecular type of hypothesis assumes the existence of distinct molecules in the crystalline state, just as in the gaseous and liquid states. It has been most elaborately developed by Smits. Having first shown experimentally that a dynamic chemical equilibrium between different kinds of molecules very probably exists in the liquid and crystalline states of certain substances, Smits' theory goes on to postulate such an equilibrium in every phase of every substance which exhibits polymorphism, and to apply thereto the well-known principles of the phase rule of Gibbs and Roozeboom.

The "structural" hypotheses assume that polymorphous forms of a substance differ simply in the arrangement of their constituent parts in the crystal lattice, whether those parts be molecules, atom-groups, or atoms (Bravais, 1851). Different orientation of the parts, without change of the arrangement in space of their geometrical centers, is also suggested as a variant of this type of hypothesis (Bridgman, 1916).

The "atomic" type of hypothesis assumes that the polymorphous change is due to a change of form of some or all of the atoms of the substance, without necessarily any change in their arrangement or orientation. The change may be in the positions or orbits of the outside or planetary electrons, or it may even affect the atomic nucleus itself.

Now it need hardly be said that all these types of polymorphism may actually exist, one in one substance, one in another; or that there may be a real gradation from one type of polymorphism to another (Rinne, 1916). The inversion of benzil-ortho-carbonic acid at 65.7° might be taken as an example of polymorphism which is clearly molecular. The inversion of pure iron at 770° may be best explained as mainly an atomic inversion.

The inversions of silica are best explained as partly structural and partly atomic. We shall therefore add the following hypotheses to the two which have preceded:

(C) *The sluggish type of inversion in silica depends upon a fundamental rearrangement of silicon and oxygen atoms.*

(D) *The high-low type of inversion in silica goes deeper into the atom than the sluggish type, but involves also a subordinate change in the relative positions of atoms.*

These hypotheses must now be particularized, in order that we may make as definite predictions as possible for comparison with experimental facts. Valuable suggestions for such particularizing will be found in the many measured physical properties of the forms.

Among the dozens of clues which might give a hint as to the explanation of the polymorphism of silica the following are particularly suggestive: (1) The coefficients of thermal expansion of the three high-

modifications are small or even negative, in which they agree also with vitreous silica; (2) the high-low inversion temperatures are inversely proportional to the specific volumes of the three low-modifications (see p. 413).

Now a mechanically compact and stable atom-triplet, capable of taking up within itself most of the thermal vibration due to rising temperature, and so constructed that it can be used as a building unit in three different ways to make three space lattices of atoms, would account for the three high-temperature modifications; then, if within each of these structures we can find an atomic binding mechanism common to all three, which mechanism is balanced against a force of thermal agitation tending to separate certain atoms in the structure, we can account for the high-low inversions and their dependence upon volume.

At the same time, various properties of liquid, vitreous, and colloidal silica suggest a *thread or chain structure.*

The next step is to combine these various specifications into a consistent whole.

Structure of the atom-triplet and silica thread

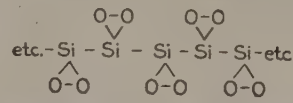
We have seen in Chapter III that the free silicon atom has 14 planetary electrons, of which 4 are external to the stable set of ten which characterizes neon; while the free oxygen atom has 8, of which 6 are external to the central pair. We have seen also how the combination between silicon and oxygen to form silica is the result of the tendency of the silicon atom to complete an octet of electrons by either losing or taking on 4 electrons, and of the oxygen atom to complete its octet by taking on 2 electrons. It has been shown, further, that this can be accomplished by the sharing of electrons between the atoms. The next question is as to the precise method of sharing.

At the close of Chapter III there was presented, in Figures III.5, III.6, and III.7, one of the simplest of the many possible ways of combining silicon and oxygen by sharing electrons. This yielded a self-contained atom-triplet which might perhaps serve to represent the structure of SiO_2 molecules in a very dilute gas, but gave no explanation for the formation of liquid, vitreous, and crystalline silica.

The hypothesis of the structure of liquid and vitreous silica now to be proposed is an attempt to provide that necessary explanation. It assumes that, when molecules of silica are brought near enough together to form a dense gas and ultimately a liquid, the silicon atom shares one pair of electrons with each oxygen, and the oxygens share a pair of electrons between them. At the same time the silicon shares one pair of electrons with each of two neighboring silicons. The result may be stated as our next hypothesis:

(E) *The fundamental building unit of silica is a silica thread built up of SiO_2 atom-triplets.*

It may be crudely represented in a plane by means of the familiar valence bonds, thus:



or by some such representation as that of Figure XV.1. This figure emphasizes mainly the ideas of grouping and sharing, without attempting to represent the distribution of electrons or atoms in space. The silicon and oxygen atoms are not all in a plane, as they are in a two-dimensional

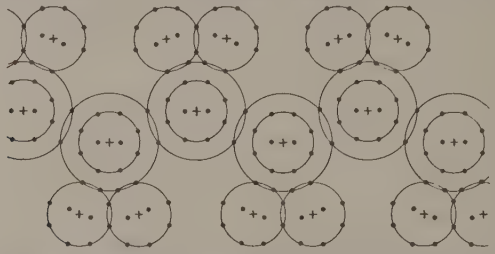


FIG. XV.1.—Plane diagram to illustrate the sharing of electrons between silicon and oxygen atoms, in a manner of combination which yields a silica thread of indefinite length.

figure, and the orientation of the oxygen pairs varies with the conditions, as will appear below.

In terms of Bohr's theory of atomic structure (see p. 38) the foregoing hypothesis assumes that in liquid silica, and possibly also in solid silica, two of the electrons in orbits of type 3_{22} added to each silicon atom come from neighboring silicons, and the other two from the two oxygens;

FIG. XV.2.—Sketch to aid in visualizing the shape of the atom-triplet SiO_2.

the two electrons of orbits 2_{22} added to each oxygen atom are drawn, one from the silicon atom, and the other from the second oxygen atom. But, as already remarked in Chapter III, the formal representation of this bonding says nothing about whether the Lewis-Langmuir type or the Bohr type of atom is being taken as the basis. That part of the theory of silica which is concerned with the structure of the triplet, and its building up into the solid modifications, would remain the same whichever type of atom be assumed.

The general shape of the resulting triplet, if three interlocking solar systems can be said to have a "shape," depends somewhat upon the manner of distribution of the electrons about the nuclei. If we introduce the hypothesis, made reasonable and probable on other grounds not peculiar to silica, that

(F) *the electrons of the outer octet about each atomic nucleus are associated in pairs,*

then the resulting three atom-structures (one silicon and two oxygens) are roughly tetrahedral, and the three are closely assembled into an atom-triplet which is roughly trigonal. The sketch in Figure XV.2 may help to visualize the shape.

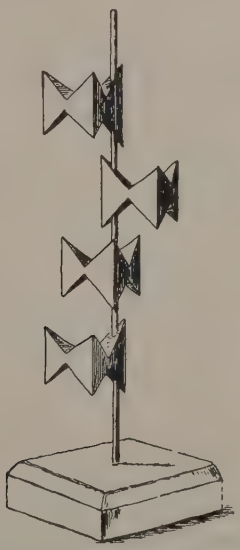


FIG. XV.3.—Sketch to illustrate the helical arrangement of SiO_2 atom-triplets along the hypothetical silica thread.

The silica threads themselves are very narrow relative to their length, for they are only one atom-triplet in diameter. Their length may run to hundreds, thousands, or even millions of atoms. A thread a million atoms long would have a length in the usual units of about 0.16 mm.

The spatial structure of the thread and its parts may be visualized with the help of Figure XV.3, sketched from the photograph of a model.

It must be emphasized here that we are no longer dealing with a purely geometric unit such as that represented in Chapter XIII by Figure XIII.6. With the help of hypotheses (A) and (E) we have progressed to the point of recognizing a real physical unit of structure.

Manner of interconnection of the threads

We have still to elaborate hypothesis (B) to explain the formation of solid modifications. That hypothesis states that "the solid state in silica is the result of the sharing or transfer of electrons between neighboring atom-triplets." Which electrons, and are they shared, or transferred, or both?

Many different arrangements are conceivable. The thread-hypothesis (E) in itself provides one kind of interconnection of triplets which might explain qualitatively the properties of the liquid and glass, simply by the tangling of the threads, but this would not account for the crystalline modifications.

Some light may be thrown on the question by a comparison of silica with the analogous compound carbon dioxide, CO_2. Both are dioxides, and both contain one atom with four outside valence-electrons.

The important difference between the two compounds lies in the fact that carbon has no internal set of eight electrons, but only its central pair and its outer four valence-electrons. It is therefore a much more self-contained atom when in combination in CO_2 than is silicon in combination in SiO_2. Silicon's inner set of eight swells it, so to speak, as compared with carbon, and its two pairs of electrons are pushed over toward the oxygen nucleus.

This produces a distortion of the oxygen structure, making it possible for an oxygen atom belonging to one thread to influence electrically a silicon atom in another thread, possibly interlocking the electron orbits of the two atoms and in effect producing a kind of chemical union between them.

We may then make the following additional hypothesis of structure:

(G) *The solid state in silica is partly due to the interlocking of electron orbits of oxygen and silicon atoms in neighboring silica threads.*

The phenomena of ultra-red reflection (Chapters XXXV, XXXVII) make it improbable that the interrelation of atoms in silica is wholly a sharing of electrons, for the reflections indicate the presence of ions of atomic size, such as would be produced by the transfer of an electron from one atom to another. At the same time it is improbable, for reasons given elsewhere, that silica is a purely polar compound. Some compromise between the two seems necessary, but our knowledge is not far enough advanced to make hypothesis (G) more definite.

With the seven hypotheses stated in preceding pages as a basis, we may now proceed to the study of the most probable structures for liquid and vitreous silica and the three principal crystalline forms: cristobalite, tridymite, and quartz.

Structures of the modifications of silica

Liquid and vitreous silica

Since the silica thread is an electron-maintained structure underlying all the solid forms, we must assume that it is present in liquid silica and that its formation may begin even in the gas. In the liquid the threads are in a constant state of vibration and movement, with the oxygen pairs in haphazard and probably varying orientation relative to the thread. A drop of liquid-vitreous silica at a temperature of 1700 to 1800° would resemble a mass of wriggling worms. The threads themselves not improbably would have a helical twist.

Most inorganic liquids, upon reaching a certain characteristic temperature known as the "melting-point," assume a symmetrical arrangement of their constituent atoms,—the process known as "crystallization". The same tendency exists in silica below 1710°, but the triplets and threads are so stable that the rearrangement into a crystalline pattern is very slow. Further, the rate of rearrangement becomes slower, the lower the temperature. Hence liquid silica, if rapidly cooled, can be brought to a state where the original heterogeneous arrangement of threads and triplets is indefinitely preserved.

Beginning in a state of activity above 1710°, the threads, on cooling, thus grow less and less active, until they become first like a tangled mass of cotton string or machinists' waste, and then, at still lower temperatures, like a compressed pad of wires, and we have solid vitreous silica or silica *glass*. An intricately tangled mass of wires has some of the properties of a solid, even though the individual wires are flexible.

This ready formation of a vitreous state is one of the phenomena which most strongly differentiate silica from the salt-like compounds. It does not accord with any hypothesis which assumes that the structure of crystalline silica is atomic and non-molecular, for in that case it should crystallize, like metals and salts, with great ease.

On the other hand, the similarity in many properties between vitreous silica, cristobalite, and quartz shows that similar types of interconnections between atoms exist in all three. The solid state of vitreous silica is therefore not due solely to the tangling of silica threads.

Thermal agitation

The kinetic theory of heat requires us to assume that at all temperatures the atoms, atom-triplets, and threads are in a state of thermal agitation. Because of the fairly rigid construction of the triplet we may picture the thermal agitation as consisting both of rotatory vibration of triplets about the axis of the thread as an axis of rotation, and of their transverse vibration perpendicular to the axis of the thread. The net effect on a given thread is analogous to the waves of movement which are seen to pass along

a rope which is fastened at one end and shaken by transverse and circular movements at the other end.

Above 1710° these irregular rotatory and transverse vibrations in the threads prevent the forces which act among the silicon and oxygen atoms from pulling the SiO_2 triplets into any definite and permanent pattern. Below 1710°, on the contrary, these vibrations aid any rearrangement which is more stable, but aid it the less effectively, the lower the temperature.

Grades of permanence in vitreous silica

The haphazard though only slowly changing arrangement of threads existing at the temperature of complete fusion thus becomes more and more fixed as the temperature falls toward atmospheric. At temperatures near the melting-point mechanical deformation is still possible. I have called this the "soft-string stage." Any deformation at this stage, such as the drawing out of a lump of glass into a rod, might naturally be expected to disturb the haphazard arrangement of the threads and give some of them a prevailing orientation parallel to the rod. This would explain the difference in expansion parallel and perpendicular to the axis in silica rods or tubes and the variation in expansion between different samples, indicated by some experiments (see p. 407). It will also aid in explaining the evidences of ribbon-like crystallinity in silica rods and tubes, observed by Rayleigh (see p. 137).

At a somewhat lower temperature we reach a stage where there still persist abnormal gaps and abnormally crowded places among the threads, as well as portions of any given thread which are abnormally twisted or abnormally stretched or compressed, but where some movements are occurring tending to equalize the irregularities. These movements constitute the phenomena of *spontaneous deformation* (see p. 474).

In a third stage, at still lower temperatures, the threads remain practically permanent, but the oxygen atoms of the triplets are still capable of moving into more stable positions. These movements form a part of the phenomena of *annealing* (pp. 459 and 768).

Finally, there is the stage at atmospheric temperatures and below, where no perceptible rearrangements of atoms are occurring, but where mechanical disturbance of the structure may have an effect mildly resembling the effect of thermal agitation, and may lead to rearrangements of oxygen atoms which receive outward expression in the phenomenon of mechanical *accommodation* (p. 477).

This theory of the structure of vitreous silica may be summarized in the following two hypotheses, which I believe will also be found applicable to any silicate glass:

(H) *Every piece of glass, as originally drawn, cast, or blown, has a structure of its own, just as a tree, sea-shell, or concretion has its own structure; this structure is the resultant of its* MECHANICAL *history.*

(J) *Superposed on the mechanical structure is a finer structure which is the resultant of the* THERMAL *history of the glass, and which can therefore be changed and brought to a fairly reproducible state by thermal annealing, but without greatly altering the original mechanical structure.*

High-cristobalite

Only above 1710° is a tangled mass of wriggling threads the most stable state which a drop of silica can assume. Below 1710°, if time be allowed for the process, and if it be not too much hindered by lowering of the temperature, the threads can be straightened out and built up into a symmetrical structure, which, when once formed, is able to resist the disintegrating action of the thermal agitation of triplets and threads. This symmetrical structure we call "crystalline".

Suppose the cold vitreous silica, described in preceding paragraphs, to be reheated to a temperature in the vicinity of 1600°, which is below the melting temperature of cristobalite, but hot enough to cause vigorous vibration. The tangled threads resume to some extent their active movements, but their thermal vibrations are so much reduced below those characteristic of the truly liquid state that certain interatomic forces begin to prevail. According to hypothesis (F), the larger size of the silicon atom as compared with the oxygen distorts the latter so that there is a residual force at the "outside edge" of each oxygen. This force tends to hold an oxygen and a silicon atom together whenever they accidentally approach one another, perhaps because electron orbits from the two neighboring atoms actually interlock during such an approach. The result is a gradual straightening out of the threads. Very crooked ones break, and fragments of different threads unite to form new and straighter threads, until the structure comes to resemble an interwoven mass of wires having three prevailing directions at right angles to one another. The result is a crystalline structure of external cubic symmetry, the modification known as *high-cristobalite*. The specific volume and the thermal expansion coefficient remain practically the same as for vitreous silica.

Since the silicon atoms in a thread are already interconnected, according to hypothesis (E), it is probable that this interconnection will persist in some form in the crystal. The primary tendency to symmetrical arrangement would come from these interconnected silicon atoms; this may explain their arrangement into the pattern characteristic of elementary silicon, the diamond pattern, which is actually found in high-cristobalite (see XIII). The oxygen atoms next move into positions half way between silicon atoms of neighboring threads, but not all of them succeed in reaching such positions. The consequences of this important departure from perfect crystallinity will be referred to again in this chapter, and repeatedly in subsequent chapters, in considering the peculiar properties of cristobalite.

The most likely position for the axis of the original silica thread seems

to be the cube diagonal, that is, the direction perpendicular to an octahedral face. As has been brought out by Beckenkamp,[4] this direction bears important relations to the symmetry of both the isometric and the hexagonal modifications of silica. Suppose the silicon atoms arranged in some variety of cubic lattice. Then imagine this structure turned up on one corner so that the octahedral normal is vertical. It may now be considered a rhombohedral lattice. For example, if the cubic lattice be a face-centered cube, its axial ratio considered as rhombohedral would be $a:c = 1:\sqrt{6}$ or 1 : 2.4495.

In the form in which this general theory was first presented[5] it was easy to convert cristobalite in this way into a rhombohedral structure which served as a basis for the construction of high-tridymite and high-quartz, and which could be converted by further small movements into structures which would fit the properties of low-tridymite and low-quartz. Now that we know something of the structure of high-cristobalite, the conversion does not seem so simple. Nevertheless some account must be taken of the hexagonal mimetic habit of high-cristobalite (see p. 56) as well as of the peculiar isometric relations of quartz and tridymite (see p. 204), and I believe the explanation will be found in the isometric-rhombohedral relationship stressed by Beckenkamp.

High-tridymite

When the temperature falls below 1470° the diminished thermal agitation permits of a more stable configuration, namely, that of *high-tridymite*. The structure is hexagonal in external symmetry. The silica threads,—assuming that they still persist through some electronic interconnection,—may lie parallel to the hexagonal axis. The structure should be allied to that of high-cristobalite on the one hand and that of high-quartz on the other, the more closely to the latter. As the tridymites are the least known of all the modifications, the structure can not be specified more definitely.

High-quartz

Further lowering of the temperature to 870° brings about still another rearrangement, producing the modification known as *high-quartz*. The structure is hexagonal in symmetry, and is definitely known (see XIII). The original silica thread I assume to have its axis, as in high-tridymite, parallel to the principal axis, and identify it with the open channel or "well" which appears in the structure as shown in Figure XIII.9, imagining the electron orbits of silicon atoms to intersect along this channel. It is through this opening that electrolytic migration of ions takes place in the axial conduction of electricity by quartz (see p. 538).

The next step is to find hypotheses which will explain the high-low

[4] Article cited in XIV, note [24].

[5] Sosman, R. B., *A theory of the structure and polymorphism of silica*, J. Franklin Inst. (1922) **194**: 741-764.

inversions and which will at the same time be consistent with the hypotheses already offered.

Theory of the high-low inversions

General theory

It has been assumed in the foregoing hypotheses that the maintenance of the crystalline structure of the forms of silica depends upon two constraints: first, the connection of the silicon atoms into threads; second, some manner of combination between the outer end of an oxygen atom belonging to one atom-triplet or thread and a silicon atom of another triplet or thread. These constraints are similar in character in all three of the principal forms.

Since the high-low inversions involve a change in structure, our next hypothesis follows naturally from the preceding, namely:

(K) *The mechanism of the high-low inversions is similar in all the forms of silica.*

The phenomena in quartz are the best known and furnish the most valuable clue to the atomic mechanism. Most, if not all, of the properties of quartz begin to change noticeably at a temperature considerably below the inversion, and the change progresses at an increasing rate up to 573° where there is a sudden jump to an entirely different curve, which exhibits no such change of rate. With falling temperature the pair of curves is reversed, except that the sudden jump comes at a slightly lower temperature.

As I have pointed out elsewhere,[6] the form of curve shown by quartz, and characteristic of type II high-low polymorphism (see Chapter VII), is duplicated exactly by the curve showing the relation between the angular velocity and the moment of the forces on two coaxial cylinders rotating in water. There is a limiting value of speed below which the moment is proportional to the speed, and above which the square of the speed enters, with a discontinuity separating the two states of motion.

An equally instructive analogy is found in the state of oscillation of two coupled oscillatory electric circuits, one of which is supplied by an electron tube.[7] In this case the curve of current against the natural frequency of the secondary circuit, when the frequency is varied continuously, not only jumps suddenly at a certain point, but jumps back at a *different* point when the conditions of change are reversed. In showing this "oscillation hysteresis" the system duplicates exactly the behavior not only of quartz, but of all the high-low inversions of silica, since all show a definite temperature hysteresis in the inversion phenomena according as the tem-

[6] Day, Sosman, & Hostetter, Amer. J. Sci. (1914) **37**: p. 19; Neues Jahrb. Min. etc. (1915) Beil.-Bd. **40**: p. 139.

[7] Van der Pol, B., *On oscillation hysteresis in a triode generator with two degrees of freedom,* Phil. Mag. (1922) (6) **43**: 700-719.

perature is rising or falling. This behavior is also duplicated by high-low inversions in iron and other substances.

Evidently some subsidiary part of the structure (triplet, atom, nucleus, or electron) is in a state of motion which varies with the temperature, but which influences the motion of some other subsidiary part in such a way that the secondary motion changes suddenly from one state to another. This performance probably does not take place mainly or entirely within the triplet, else all the forms of silica would have an inversion at about the same temperature. On the contrary, the inversion temperature is inversely proportional to the volume of the low-form.

I have therefore assumed that the high-low inversion affects chiefly the outside linkage between oxygens and silicons which, under the present theory, is one of the two constraints holding the crystal together. We have then this hypothesis of the high-low inversion:

(L) *The high-low inversions in silica consist* (*with rising temperature*) (*a*) *in an increase of amplitude of the thermal vibration of a pair of atoms, which* (*b*) *influences the manner of revolution of a pair of electrons, with the result that* (*c*) *a relatively constant attraction between the two atoms becomes balanced by an increasing repulsion between the two orbits in question.* At a certain temperature the existing structure becomes unstable and the atoms move suddenly to a new position characteristic of the high-form.

Furthermore, it seems likely, from the discussion of the structure of low-quartz in XIV, that the largest displacement relative to the structure as a whole is a displacement of oxygen centers, not of silicon centers.

Until we learn more about the probable form and distribution of the 32 electron orbits which we assume to exist in each triplet, it will not be possible to specify more exactly the character of the change in the orbital motions. Perhaps it consists in the production of rotational vibrations of the plane orbits of an electron-pair, which vibrations become actual rotations of those planes at the inversion-point. This would be a possible electron mechanism to explain Ashworth's theory of the high-low inversion in iron. Experiments on the effect of an A. C. field upon the magnetic properties of quartz through the inversion-point might throw light on this question.

The foregoing hypotheses may now be applied to each of the principal forms of silica in turn.

The high-low inversion in cristobalite

Cristobalite exhibits the unusual property, which Fenner was the first to observe in silica, of a variable inversion temperature. The higher the temperature at which the cristobalite was formed, the higher is its high-low inversion-point. The explanation of this property evidently calls for some kind of structure which changes at high temperatures but which is

preserved at lower temperatures and is not affected by the inversion. I believe it is best provided by the following hypothesis:

(M) *The structure of cristobalite is incomplete; part of the oxygen atoms are in undefined or haphazard positions.*

The variable inversion temperature may then be accounted for by the following supplementary hypothesis:

(N) *The proportion of haphazard oxygen atoms in cristobalite increases with the temperature, and is preserved by rapid cooling to temperatures of 300° or lower.*

Low-cristobalite has a density intermediate between the densities of low-quartz and low-tridymite. It is reasonable to suppose, therefore, that the average distance of oxygen and silicon atoms in low-cristobalite is intermediate between that in quartz and that in tridymite. Hence its inversion temperature is also intermediate (200 to 275°). The variable proportion of haphazard oxygen atoms, then, varies slightly their average separation and causes the inversion-point to occur at different temperatures within a range of 75°, varying with the previous thermal history of the specimen.

Another unusual feature of the cristobalite inversion is the fact that the high-modification breaks up into such a large number of differently oriented crystals of the low-modification. It has already been remarked in Chapter VII that this cannot be simply the result of a large volume-change at the inversion, because the considerable volume-change in quartz at 573° does not have any such effect. An additional hypothesis is necessary to account for this fact, and the following is one which is consistent with those that have preceded and even follows logically from them:

(O) *The structure of high-cristobalite is heterogeneous on a submicroscopic scale.*

The heterogeneity assumed is of a kind which would not be evident optically, unless perhaps in the scattering of light (see Chapter XXXVIII). It would consist in the presence within the crystal of variously-oriented favored directions,—not the definitely determined directions proper to the symmetry, but directions unpredictable by any means except a theory of probability. We might imagine these directions to coincide with silica threads which have greater length or higher symmetry than other threads, and which serve as nuclei or rather cores toward which all the atoms within a radius of several hundred or thousand atoms tend to move when the high-low inversion occurs. These favored directions determine the position of the axes of the innumerable crystals of low-cristobalite which result from the inversion of the original single crystal of high-cristobalite.

High-low inversions in tridymite

In the tridymite structure the atoms are, on the average, farther apart than in cristobalite, and the mutual influence of their electron orbits is less.

A smaller increase of temperature (to only 117°C) is therefore sufficient to break up the interlocking which is characteristic of low-tridymite and convert it into the type which is characteristic of the high-form.

The high-form itself, however, has two modifications, an upper and a lower, with an inversion at 163°. This 163° change gives a very small heat-effect, and is probably only a final step in completion of a principal change which occurred at 117°. An explanation for it may possibly be found in a structure in which there are two kinds of association of atoms or two characteristic inter-atomic distances which are nearly but not quite equal. But not enough is known of the symmetry and other properties of low-tridymite, or of the differences between the upper and lower high-tridymites, to warrant the construction of models for these modifications.

Low-quartz

In applying our hypotheses, finally, to quartz, we come as near as is possible at present to getting our feet on the ground, since quartz is the form on which the largest amount of structural evidence is available. This evidence has already been described in Chapter XIII, and the most likely structures consistent therewith have been discussed in Chapter XIV. It was shown there that the space-lattice of both modifications of quartz is hexagonal, and that the smallest repeating unit consists of 3 SiO_2 atom-triplets, each rotated 120 degrees about the principal axis with respect to its predecessor along the direction of that axis. The exact positions of silicon and oxygen atoms in the unit cell, requiring a knowledge of four parameters, could not be finally determined.

According to Bragg and Gibbs, the change in structure of high-quartz which converts it into the low-modification and is in best agreement with the intensities of X-ray diffraction consists in a rotation about the principal axis of the triangle made by a silicon center and two neighboring oxygen centers. According to Beckenkamp, the change which is in best agreement with the face-development and optical properties is a movement of oxygen atoms only, so far as relative position of atoms is concerned.

In either case we may suppose that as the temperature rises the increasing amplitude of vibration of the atoms finally brings about a sudden change in the mode of revolution of certain electrons associated with a pair of atoms, just as in tridymite and cristobalite. The atoms are nearer together, however, in quartz than in the other forms, hence a greater increase of temperature,—to 573°C—is necessary to bring about the change.

Vitreous silica

In hypotheses (K) and (L) on the mechanism of the high-low inversions nothing is said which implies that the SiO_2 triplets and the interacting atoms must be part of a *crystalline* structure. We must then inquire what

will be the conditions for a high-low inversion in vitreous silica. The solid character of vitreous silica is assumed to be due primarily to the existence of long silica threads and their entanglement, and only secondarily to the interconnection of atoms. Many paired oxygens and silicons can doubtless be found, but their distances apart must vary continuously over a wide range of values. Accordingly, the high-low inversions in those pairs are scattered over a range of temperatures and no marked effect is discernible at any one temperature.

Extension of the theory to silicate systems

If the foregoing hypotheses are true as regards the self-containedness of the SiO_2 triplet, its association into threads, its threefold upbuilding into crystalline modifications, and the intimate nature of its high-low inversions, then they should be capable of extension into the theory of systems of which silica is a component. This is not the place to take up such an extension in any detail, but a few scattered applications will serve to show that the theory may be profitably adapted and extended to silicate systems in general.

In the system $SiO_2:H_2O$ the thread hypothesis seems capable of accounting for some of the properties of colloidal silica. A stiff silica gel, for instance, may be pictured as something like a wad of cotton saturated with water.

The polymorphism of the silicates offers many interesting suggestions. The threefold sluggish-type polymorphism of silica is duplicated in the three forms of potash feldspar ($KAlSi_3O_8$) and possibly in soda feldspar ($NaAlSi_3O_8$), magnesium metasilicate ($MgSiO_3$), and other silicates. The negative expansion coefficient of high-quartz appears in two of the axes of the highly siliceous soda and potash feldspars (Fizeau). The high-low inversion curve of quartz is duplicated in detail by a similar high-low inversion in leucite at a slightly higher temperature. Several investigators have reported evidence of relatively rapid changes in the properties of complex glasses between 400 and 600°, which may be related to the high-low inversion of pure silica. And so on. These are scattered examples among the silicates of phenomena whose explanation must take into account the theory of polymorphism of silica itself.

Analogies with other elements of Group IV

The foregoing hypotheses have been based in part upon an atomic structure for silicon containing 4 external planetary electrons, that is, 4 electrons in a group having orbits of the highest quantum number. We must expect then that other elements having a similar external structure will show similar chemical phenomena.

There are some suggestive analogies between the properties of silica

and those of the dioxides of the other tetravalent elements close to silicon in the Periodic System. The four oxides, TiO_2, GeO_2, ZrO_2, and SnO_2 are all solid oxides of high melting-point, which combine with water to form colloidal hydrates, and with basic oxides to form solid compounds (titanates, germanates, zirconates, stannates) showing many resemblances to the silicates. The analogies in their polymorphism are equally suggestive. TiO_2, the best known of the four, exists in three polymorphous forms, each of which has a temperature range of stability, like the three forms of SiO_2. SnO_2, likewise, exists in three forms which appear to be isotrimorphous with the forms of TiO_2 but whose properties have not been determined with certainty. Much less is known of ZrO_2, of which two forms are on record; while GeO_2 has scarcely been studied at all and the desired data are wholly lacking.

High-low inversions occur in all three forms of TiO_2 and in the cassiterite form of SnO_2, as is revealed by heat-capacity determinations.[8] Further search for such inversions in all the dioxides mentioned should yield results of interest.

Summary of the theory

The foregoing theory of the structure and polymorphism of silica may now be summarized as a whole, before we pass on to its applications in explaining the relationships and properties of the modifications of silica.

The theory has been called forth by the wide variety of experimental data which we possess on the forms of silica, particularly quartz, and which have never been assembled and explained on the basis of a unified and consistent set of hypotheses as to the ultimate structure of the substance. This chapter attempts to provide such a set of hypotheses, based upon the general knowledge which we have already gained concerning the structure of matter in general and that of silica in particular.

It is believed that the silica atom-triplet maintains some degree of individuality in its amorphous and crystalline states. The freedom of its oxygen atoms to change their positions with respect to the silicons is restricted, as is shown by the impossibility of changing right-quartz into left-quartz. The triplets are assumed to assemble into chains or threads in the liquid and glassy states, and a thread structure may persist in the crystalline states. The three principal crystalline forms (cristobalite, tridymite, quartz) are built up by combining the threaded triplets in three different ways, the connection between threads being through the external electrons of oxygen and silicon atoms.

The high-low inversions in all the three forms are thought to be due to the same underlying mechanism, namely, a change in the state of motion of certain electrons, resulting from the change of thermal vibration of the atoms with temperature, whereby the shape of the silica triplet and

[8] Lashchenko, J. Russian Phys. Chem. Soc. (1910) **42**: 1604-1614.

the relative positions of two atoms are suddenly altered as a result of the passage of the system through a stage of instability.

The variability of the inversion-temperature of cristobalite is thought to be due to the existence, in varying proportion, of atoms in random or undefined positions within a structure which is as a whole orderly or crystalline.

The properties of vitreous silica and of silicate glasses in general are assumed to depend upon the existence within such glasses of two types of structure, namely, a coarse structure depending upon the mechanical history of the fragment under consideration, and a finer structure, superposed on the first, depending upon the thermal history of the fragment.

The theory as a whole gives a satisfactory explanation for many phenomena of silica which have not yet been discussed in this book, but which are taken up in their turn in later chapters in which the properties of silica are more fully presented.

It must not be supposed that the theory offered in this chapter is the product of a single line of logical reasoning based solely upon the facts already given. Scientific theories do not grow that way. A scientific theory resembles rather a political party's platform in being a severely trimmed and frequently readjusted combination of pre-existing theories with a little new material designed to shape the whole into a consistent form which will stand the vicissitudes of the near future, pending the development of something more convincing.

A sketch of the development of some of these pre-existing theories and a comparison with other hypotheses which are under discussion at the present time will be given in Chapter XVII.

Chapter XVI. FURTHER APPLICATIONS OF THE THEORY

We may now further elucidate the theory of structure and polymorphism of silica which forms the basis of this book, by applying it to some of the facts already presented in Chapters IV to XII.

The sluggish inversions

If we consider qualitatively the crystalline structures proposed for high-cristobalite, high-tridymite, and high-quartz, their ease of formation would seem to be in the order just given. High-cristobalite, formed by the arranging and straightening out of silica threads but not requiring that all oxygen atoms of the triplets shall be in exactly defined positions, should form relatively easily. Next in the stage of complexity would come high-tridymite, to produce which the SiO_2 triplets must all be rotated into symmetrical positions about the axis of the silica thread and all the oxygen atoms also be placed in defined positions. To produce high-quartz, the triplets must be further rearranged in such a way that the oxygens and silicons have a helical arrangement about the thread axis.

The reason is now clear why vitreous silica, in devitrifying, always forms cristobalite, even at temperatures below the true cristobalite range. Tridymite and quartz have never been made directly from the glass, except with the aid of a solvent which can take the silica triplets into solution so that they can redeposit in the more complicated structures.

Transformations of cristobalite

Once formed, cristobalite may be expected to change more readily into tridymite than into quartz, but into either only with difficulty. The facts so far as known are in agreement with these expectations.

Transformations of tridymite

Tridymite, on the other hand, might at first sight be expected to change more readily into cristobalite than conversely. But here enters another factor. The completed structures of tridymite and quartz should be very resistant to the disintegrating effects of a high temperature. When they do disintegrate, the threads may be expected to fall into the heterogeneous assemblage which characterizes liquid or vitreous silica rather than into the partly completed structure of cristobalite. In other words, the cristobalite structure is approached more readily from the disordered than from the regularly oriented side. We therefore find that at 1670° tridymite melts to vitreous silica more rapidly than it changes to cristobalite.

For the same reasons the change of tridymite into either vitreous silica or into cristobalite should be more rapid than its change into quartz, and this is found to be the case.

Transformations of quartz

As with tridymite, so with quartz the line of least resistance to the disintegration of the crystalline structure by high temperatures seems to be through the disordered structure of the vitreous state. After the glass is formed, the threads then begin to arrange themselves into the more orderly pattern of cristobalite.

The difficult rearrangement of quartz into tridymite takes place only with the aid of a solvent.

General course of the transformations

The data and theory may be graphically summarized in some such manner as is shown in Figure XVI.1. With the symbols arranged as shown, the route of least resistance is, in general, clockwise.

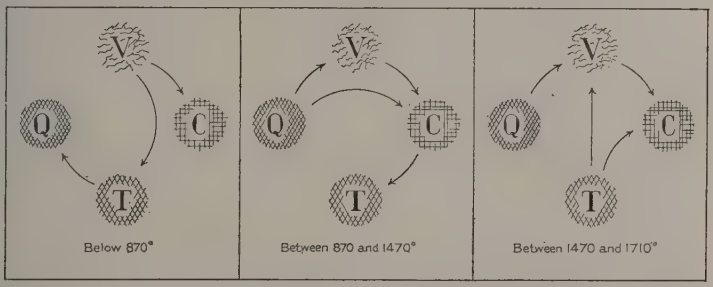


FIG. XVI.1.—Routes of least resistance in the transformations of silica.

Vapor pressure

The low vapor pressure of silica indicates polymerization. This is in accord with the theory, the polymerization consisting in the formation of silica threads of indefinite and varying length.

Carbon dioxide, which is the simplest chemically analogous compound in Group IV of the Periodic System, and which is presumably not polymerized in its solid state, has a much higher vapor pressure at a corresponding temperature, that is, an absolute temperature which is the same fraction of the critical temperature.

Surface effects

From the stability of the quartz and tridymite structures it is natural to infer that the transformation to the vitreous or to the cristobalite structures could begin only with difficulty in the interior of the crystal. At the surface, on the contrary, there is much greater freedom of movement, and broken and distorted threads may be found there. Hence the change

should begin at the surface. This is well known to be true of quartz, while on tridymite observations are lacking.

The effect of the surface seems to extend to the composition-surface between the units of a twinned quartz crystal. This is indicated by the rates of conversion of twinned quartz into cristobalite, referred to in XI.

The effect of free surfaces is also felt in the devitrification of vitreous silica to cristobalite, a process which begins most actively at the surfaces of fragments, if fluxes are absent.

Surface catalysis

Increased freedom of movement at the surface may not be the whole explanation for the formation of cristobalite at the surface of quartz and vitreous silica. In vitreous silica it would seem that the rearrangement could also begin in the interior, and there is evidence that it does, in the "rotting" of the glass by high temperatures without its complete conversion to cristobalite. But it does undoubtedly go much faster from the surface.

I have suspected that the oxygen and the water vapor of the air may have something to do with initiating changes at the surface of quartz or vitreous silica. The accelerating effect of water vapor in considerable quantity has already been recognized. Both O_2 and H_2O are adsorbed on silica, perhaps by direct combination of oxygen to oxygen. The resulting surface complex might be more easily rotated into a new position than the triplets and threads alone, which have unbalanced attractions to their underlying neighbors of similar kind.

When experimenting with the oxides of iron Mr. Hostetter and I observed several times that the vitreous silica insulating capillaries of our platinum-platinrhodium thermocouples seemed to remain vitreous after being heated in a vacuum at temperatures where we had been accustomed to see them fall to pieces by devitrification when heated in air. We therefore made a note to try the effect of oxygen on the devitrification of the glass, because it may have been possible that the resistant capillaries were simply a better fused and therefore more resistant glass than the capillaries which had gone to pieces in air. But change of occupation during the War postponed these experiments along with a good many others.

It may be of interest to mention here the tradition that a sulfur-bearing coal, when used for firing a kiln of silica brick, produces more rapid conversion of quartz into cristobalite than a sulfur-free coal. Sulfur has the same outside electron structure as oxygen and may therefore be expected to act similarly if adsorbed on the surface of quartz. So far as I am aware, no controlled experiments have been made on this point.

Applications of the theory to the high-low inversions

Some of the phenomena of the high-low inversions have already been explained in terms of the theory in the course of its development in Chapter XV.

The most unusual phenomena of the high-low inversions of silica are those shown by cristobalite. It has already been remarked that a variable proportion of haphazard oxygen atoms, such as is called for by the special hypotheses (M) and (N) dealing with cristobalite, will cause the average temperature of the inversion to be likewise variable.

The direction of this variation cannot yet be predicted. According to the theory, the inversion-temperature is influenced by the distance apart of the atoms which are interconnected in pairs. Now the higher the temperature at which the cristobalite has been brought to equilibrium, the greater the proportion of haphazard oxygen atoms, but the effect of this changed proportion upon their average distance apart is unknown.

Nevertheless, the effect of the changing proportion of haphazard atoms upon the form of the inversion curve can be predicted. In the first place, the very existence of such haphazard atoms means that atomic pairs will be variously spaced and not all of them will invert at the same temperature; the inversion-curve of each inverting unit will be drawn out and rounded off, and given the form of type III (see Chapter VII). If we suppose that all the inversion centers assumed in hypothesis (O) are exactly alike, they will all invert at the same time and the curve of the whole will be of type III. If we suppose that they differ a little, on the average, from center to center, they will invert at slightly different temperatures and the aggregate will yield a curve of type IV. In either case we shall have a curve of the general form known experimentally to be characteristic of cristobalite.

The "inversion-temperature" determined by a time-temperature curve (the method used by Fenner) is therefore only a mean value, or a temperature near which most of the pairs invert.

Two other predictions can be made. It is reasonable to assume that the greater the proportion of haphazard atoms, the wider the range of spacings in the atom-pairs which are responsible for the high-low inversion. Therefore, the higher the temperature at which the cristobalite was brought to equilibrium, (a) the more rounded the inversion curve and (b) the wider the range of temperature hysteresis. There are not sufficient data available to test prediction (a), but (b) is in agreement with Fenner's observations.

The hypotheses of the structure of cristobalite form perhaps the most radical part of the theory of silica as presented in this chapter. I know of no facts in opposition to them, but they involve an unusual assumption, namely, that it is possible to have a crystalline substance in which not all the atoms are in geometrically defined positions. With apologies to specialists in phase rule and thermodynamics, it might be crudely called a "solid solution of a glass in a crystal." From another point of view it might be regarded as a very stiff "liquid crystal." But without the aid of the atomic theory these terms can not lay claim to any very precise meaning.

If later X-ray work on cristobalite should prove this assumption impossible, then some other mixed structure must be found which changes at high temperatures but is preserved by rapid cooling and at the same time is unaffected by the inversion.

At present it appears likely that a somewhat analogous assumption will have to be made to explain the structure of certain other substances. For example, the hydrogen atoms in NH_4Cl and in ammonium alum, $NH_4Al(SO_4)_2.12H_2O$, apparently either occupy haphazard positions or are placed in such a way that their symmetry does not conform with the symmetry of the crystal as a whole.[1]

The hypothesis of wandering oxygen atoms may help to account for the anomalous intensities of X-ray lines from high-cristobalite, observed by Wyckoff (see p. 211). He had to assume that the scattering power per electron in oxygen is considerably less than the scattering power per electron in silicon, while in most crystalline substances the scattering per electron is found approximately constant.

But if some of the oxygen atoms are missing from their places in the structure, the discrepancy might be accounted for. If this explanation is correct, then the departures from the calculated intensity ought to be found different,—probably less,—in cristobalite made at 1100° than in cristobalite made near 1600°. The only specimen examined by Wyckoff was one made at 1560°.

Quartz

The interconnection of the two oxygen atoms of each SiO_2 triplet, called for by the hypothesis at p. 250, has important consequences in the structure of quartz. If not so interconnected, they might change their positions independently, and it is conceivable that a relatively small movement of each oxygen atom could change the pair from one side of a silica thread to the opposite side. Interconnected, they can move only as a pair, and the pair would have to be rotated about the axis by 180° to change from one side to the other.

To convert right-handed low-quartz into left-handed low-quartz the pair would have to be rotated 180° and the plane of the pair with the silicon atom would then have to be given a very different inclination to the principal axis by a second movement. This means that the conversion of right-low-quartz to left-low-quartz, or the reverse, should be very difficult if not impossible. This is in agreement with experimental fact, for the one kind cannot be converted into the other except by completely destroying the structure, as for instance by dissolving it in a suitable liquid.

The same holds true of the atomic movements taking place at the high-low inversion. Right-high-quartz always remains right-handed on cooling. Although it sometimes becomes twinned, the twinning is always of the

[1] Wyckoff, R. W. G., *Structure of crystals* (1924) pp. 210, 363; Amer. J. Sci. (1922) **4**: 469-475; Ibid. (1923) **5**: 209-217.

Dauphiné type, in which all the individual parts are right-handed or all left-handed, and never of the Brazil type, which is alternately right and left.

The atoms or atom-groups in quartz evidently undergo very little if any differential movement during the inversion. This is shown by the constancy in planeness and reflecting power shown by a polished optically flat plate before and after the inversion. Even though twinning occurs, converting what was a crystallographically homogeneous plane into a series of crystallographically different planes, the reflecting power and planeness persist.

A differential displacement of atoms amounting to but a small fraction of an atomic diameter might, if repeated from atom to atom across a plate several mm wide, produce an easily visible variation from planeness. But no such effect is observed. Equally active movements of the atoms in a glass would probably produce visible permanent distortion of the polished surface.

The phenomena of varying reflection, temporary double refraction, etc., at the inversion-point are shown by Mügge's experiments to be due, at least in part, to stresses set up in the plate or crystal as a result of a slight time lag in the inversion in different parts of the piece. If the temperature gradient is great enough the stresses break the plate, otherwise they temporarily bend and twist it. There is no real differential movement of the atoms or atom-groups large enough to account for the effects.

An exception to this statement must perhaps be made for the plane parallel to the base. Mügge found repeatedly that when a plate parallel to the base has been heated and cooled through the inversion, its etch-figures come out considerably larger than before it was heated. Evidently slight changes of structure were caused by the inversion, of similar magnitude to the differences observed between different specimens and sometimes between different parts of a given plate.

These facts are all in accord with the theory. The high-low inversion is, in effect, only a simultaneous change of shape of all the SiO_2 triplets, with little if any relative displacement of the centers of those triplets. The small movement of the oxygen atoms, in which most of this change of shape consists, is felt principally in the direction of the principal axis, and its effect, if visible at all, would be most likely to appear in the basal plane. This is found to be the case.

The irregular curving nature of the composition-surfaces between the units of a Dauphiné twin lends support to the general hypothesis that the high-low inversion is due solely to a change in shape of small atom-groups.[2] If the inversion were due to a change in the space-pattern as a whole there would be displacements of such a character as to cause fracturing along any kind of a bounding surface excepting a plane or a set of planes. But if there be only a change in shape of small atom-groups, the change can

[2] MÜGGE, article cited in VII, note [3].

occur in all kinds of bays and hollows of a curving surface without producing any mass displacements and resultant fracturing.

Theory of the birefringent glass

The birefringent granules and ribbons in vitreous silica (see Chapter VIII) especially the glass studied by Rayleigh, are best interpreted as residual crystalline structures, parts of the original crystal where the silica threads, with their symmetrical disposal of SiO_2 atom-triplets about a straight axis, have not been de-oriented sufficiently to destroy entirely their power of resolving a light ray into polarized components.

They can not, of course, be regarded as simply ribbons or grains of quartz. The birefringence is too small and there is no evidence of the large strains which would be introduced by the difference in dilatation between quartz and glass. The effects produced by true residues of quartz are easily recognized, as shown at p. 94.

They also can not be regarded as consisting of threads of quartz which are nearly but not quite untwisted. Such a ribbon would be a positive crystal, while Rayleigh found the actual ribbons to be negative. Tridymite, also, would be positive.

The ribbons may, however, have the structure of cristobalite. Cristobalite resembles the ribbons in being negative, and also in having a very small birefringence.

If we make this assumption, the thermal behavior of the ribbons and granules can be explained on the basis of the theory of silica already outlined in Chapter XV.

Parts of the glass which have not been much disturbed during the fusion will be found to contain silica threads in very nearly their original position. Although the temperature has been so high that the quartz structure has been broken down, the symmetry of arrangement of silicon atoms along certain groups of threads is sufficient to permit of the easy formation of a cristobalite structure. It is likely to be a diluted cristobalite structure, shot through with threads of amorphous character, that is, threads which are bent, twisted, and characterized by triplets in haphazard orientation. This diluted cristobalite gives rise to the granular birefringence.

When the glass is drawn into rod or tubing, the localities of diluted cristobalite draw out into ribbons like the rest of the glass, and the silica threads tend to assume a prevailing direction parallel to the ribbon. The partial alining of the amorphous threads accentuates the cristobalite structure already existing and produces the biaxial crystalline ribbons.

We have seen that according to the theory a fairly permanent mechanical structure is given the glass early in its history while it is above or not far below the melting point of cristobalite. These crystalline ribbons have now become a part of this mechanical structure and are difficult to remove

by neating. They can be destroyed only by temperatures well above 1710°, temperatures which Rayleigh evidently did not attain, and are even more difficult to destroy than the granular birefringent portions, because of the additional symmetry given to the ribbons by the drawing process.

But the theory also states that a thermal rearrangement may be superposed on the fairly permanent mechanical structure, this thermal rearrangement consisting mostly in a movement of the oxygen atoms of the triplets. Most of the birefringence is due to the oxygen atoms. Hence if the oxygen atoms can be sufficiently de-oriented by heat treatment the birefringence can be greatly reduced, and in the case of the birefringent glass, where it is already very small, it may be brought down practically to zero. But since the fundamental thread structure still persists, some different heat treatment may be capable of restoring part or all of the original symmetry of position of the oxygen atoms and so of restoring the birefringence. This seems to have been what happened in the heating experiments on the disks.

The removal or restoration of the symmetrical oxygen arrangement carries with it the removal or restoration of a certain amount of general strain, because the underlying mechanical structure remains unchanged. In the disks this accompanying strain was fairly large and easily recognized because of its distribution in rings.

This is not a complete explanation of the puzzling behavior of the granular birefringence as observed by Rayleigh. It is plain, however, that his two kinds of heat treatment are decidedly different. One consists of heating at a steady temperature of about 1000° for two hours, followed by quenching. The other consists in repeated heatings at 1000° of a few minutes each. The net results of these two will differ, being in each case an integrated effect due to a whole series of temperatures from 20° to 1000°. But I believe that the theory will furnish a clue, which might be followed with greatest chance of success by studying the change of birefringence in the furnace itself while the glass is at a constant temperature.

The objection may be made to the foregoing application of the theory that if the granular birefringence which we have been calling "crystallinity," and the broad-ring birefringence which we have been calling "strain," are both due to one and the same movement of certain atoms, then there is no reason for making any distinction between the two kinds of birefringence. Both might just as well have been called "strain" in the first place.

But the same may equally well be said of birefringence in general. There is nothing about the radiation itself which will tell an observer who is ignorant of its source and path whether a given ray has been polarized by passing through a birefringent crystal or through a piece of ordinary strained soft glass. In both cases the effect is due to distorted or naturally unsymmetrical atoms or atom-groups. Nevertheless we constantly make a practical distinction between the two effects, and ascribe to "strain" any

birefringence which can be changed by means of artificially applied mechanical stresses in a way easily predicted. So with the vitreous silica disks, we can change the broad-ring birefringence in an easily predicted way by simple radial compression, while the granular birefringence remains unaffected thereby.

Theory of structure and polymorphism of the micro-forms

The micro-forms of silica are almost always fibrous, seldom granular, and never platy. This is in accord with the thread hypothesis, according to which the primary connection between SiO_2 atom-triplets is from silicon to silicon, leading to the formation of long fibers. This tendency gives rise both to the micro-fibrous crystalline varieties usually included under the general name of "chalcedony," and to the micro-fibrous amorphous varieties such as deposit from vaporized silica.

It will be evident from the data presented in Chapter X that chalcedony can not properly be called a simple "variety" of quartz.

Athough some chalcedonies, if not all, seem to contain atomic structures identical with those of quartz, the mineral departs too much in microscopic structure, rates of inversion, etc., to be considered nothing but quartz in a finely subdivided state. Furthermore, chalcedony also differs measurably from quartz in its density, heat capacity, and refractive properties.

Another important difference appears in the phenomena of the high-low inversions. The absence of any strongly marked thermal effect near 573°, and the absence of any sudden change in the birefringence of a thin-section at any temperature between 100 and 820°, show that chalcedony also differs from quartz in its high-low polymorphism.

Nevertheless a high-low inversion does exist, and betrays its close affinity to that of quartz by terminating at about 573°, although so spread out over a rather long range of temperature that it gives no such sharp change of properties as is shown by quartz.

These and other facts are all taken account of in the following hypothesis as to the structure of chalcedony:

(A) *Chalcedony is a submicroscopic mixture of fibers of quartz with interstitial amorphous silica; a variable amount of water is also held among the fibers, but is not essential to the mineral.*

It is possible also that there are chalcedonies containing interstitial tridymite or cristobalite, or chalcedonies in which fibrous tridymite or cristobalite is the principal constituent. As many as 12 such combinations are logically possible. As yet there is not sufficient evidence to say whether or not these possible variants ever occur in nature.

The following additional hypotheses will serve to explain the high-low polymorphism of chalcedony:

(B) The diameter of the fibers in a given specimen of chalcedony is variable, from about 1000 atomic diameters down to the ultimate silica thread described in the theory of silica in XV.

(C) The variable diameter of the fibers causes the high-low inversion in chalcedony to be spread over a range of temperature beginning somewhere below 573° and ending at 573°.

This hypothesis is independent of any explanation that may be accepted for the high-low inversion in general. If the theory of Chapter XV be introduced we have the following hypothesis:

(D) The variable distance between oxygen and silicon atoms along the boundaries of the fibers causes the high-low inversion of chalcedony to be spread over a range of temperature ending, with rising temperature, at 573°.

Transformation of chalcedony to cristobalite

At temperatures of 1200 to 1400° the rate of transformation of chalcedony into cristobalite is much greater than the rate of transformation of quartz. This fact is in line with the relation already brought out at p. 67, according to which the rate of transformation of quartz into cristobalite increases rapidly as the free surface of quartz is increased, whether artificially, by fine grinding; or naturally, by twinning. According to the hypothesis (A), just stated, chalcedony consists of finely fibrous quartz intergrown with amorphous silica, and it should therefore transform even more rapidly than twinned quartz. This is found to be the case.

The first effect of heat on chalcedony and flint is to drive out the water molecules which are held among the atom-triplets of SiO_2 in the inter-fiber amorphous cement. These molecules leave behind them spaces of atomic dimensions, too small to be filled by a liquid used in measuring density, yet totaling enough to make the density and refractive index of the product abnormally low. This is perhaps the principal reason for the formation of the unknown products of intermediate refractive index observed by Washburn & Navias (see p. 171). Another change which will help to account for this preliminary lowering of density and index is the simultaneous rearrangement of part of the SiO_2 triplets into the cristobalite pattern, the change ceasing as soon as the water, with its activating influence, is gone. This explains also the permanence of the product at 800°, following its formation during the first part of the heating.

When heated above 870° the silica triplets tend to rearrange themselves, first into the cristobalite pattern, then into that of tridymite, while above 1470° they change into the stable cristobalite pattern, following the course described in the theory of the mechanism of the sluggish inversions in Chapter XV. There is a considerable volume increase associated with either change, hence the constituent fibers in the more compact micro-forms do considerable pushing and sliding among themselves. The result is a large number of interspaces which are only of atomic size, yet are slightly larger than would exist were the fibers interconnected in an orderly manner into a continuous phase. Thus is brought about the low density of the cristobalite produced from the finely fibrous micro-forms such as chalcedony.

Chapter XVII. OTHER HYPOTHESES, PAST AND PRESENT

General theories of the structure of silica

Theories regarding the structure of silica are as old as science itself. One of the first scientific hypotheses on record is the one recorded by Pliny, that rock crystal is a permanent and unmelting form of ice. This is a perfectly legitimate hypothesis, just as good as any of ours of today, when we take into account the facts then available. Quartz in well-developed crystals looks like ice to the casual observer, is transparent and colorless like ice, and is commonly found in the high Alps where ice and snow abound throughout the year and the weather is sometimes extremely cold. Therefore quartz probably *is* ice which has been unusually thoroughly frozen.

This theory stood for centuries, because most of the world was ruled by authority and the rest by logic, and experiment was not in high favor.

Once the experimental method had become established, facts accumulated rapidly, and hypotheses became numerous and short-lived. To sketch the evolution of modern hypotheses on the constitution of silica would be to review the whole history of chemical and physical theory, a task already well done by Victor Meyer, Muir, and others. Only the more recent stages of this evolution, as applied particularly to silica, need be reviewed here.

One of the earliest theories arising out of the discovery of the two new forms of silica and their comparison with quartz was put forth by Mallard [1] in 1890. He suggested that quartz, with its uniaxial character and its rotatory power, might be considered as built up of biaxial units of molecular size. The same fundamental substance would form the structural unit of chalcedony, unless chalcedony itself might be considered identical with that hypothetical substance.

Mallard suggested also that cristobalite might similarly be considered as produced by the grouping (groupement) of tridymite units of molecular size. He did not commit himself as to whether the grouping is a case of twinning. The small birefringence of cristobalite is in agreement with Mallard's view.

No hypothesis was offered by Mallard for the high-low inversions. He did, however, point to the persistence of an inversion as being in agreement with the idea that cristobalite is a grouping of tridymite units, commenting at the same time on the change which this grouping causes in the temperature of the inversion, but offering no explanation of the change.

In recent years the most active contributor to the general theory of silica has been Beckenkamp.[2] In his discussions of hypothetical structures

[1] Article cited in IV, note [28].
[2] Articles cited in XIV; also a series of 5 privately published pamphlets (1926).

for the forms of silica, Beckenkamp has laid special stress on the relationships between the hexagonal symmetries of quartz and high-tridymite on the one hand, and simple isometric symmetries on the other. These relationships have already been described in Chapter XII. Beckenkamp makes the general suggestion that a hypothetical tetragonal form of silica, not identical with cristobalite, and having the axial ratios 0.57735 : 1 : 1, may be made the basis of all the structures. The dimensions of quartz can then be reproduced by shortening the third axis of this basic form, while those of tridymite can be reproduced by lengthening the first and second axes of this same basic form.

This and similar hypotheses must now stand the test of X-ray analysis of crystalline structure, but the data on silica are as yet far too incomplete to permit of a conclusive answer to questions concerning the interrelations of the forms, else these theoretical chapters need not have been such a patchwork. Nor can we be sure that the X-rays will ever be able to give a complete answer. The early results obtained with the rays were so surprising and so convincing that the chemist and the crystallographer were swept off their feet, and came near forgetting that they possess facts and relations which the physicist only imperfectly appreciates, and which he has not yet successfully attempted to explain. Nevertheless, the best promise of success seems to me to lie along the physicist's present course.

The crystalline state

The relation of silica to current views of the structure of crystalline matter may be illustrated by reference to a general article by Friederich.[3] He suggests the following classification of crystalline solids, based on the activity of the electrons within the crystal-lattice:

(a) Inert gas atom-lattice. Example, solid argon.
(b) Molecule-lattice. Example, solid CO_2.
(c) Ion-lattice. Example, NaCl.
(d) Atom-lattice without conductivity. Example SiC.
(e) Atom-lattice with conductivity due to free valence electrons. Example, metals.
(f) Atom-lattice with conductivity due to core electrons. Example, PbO_2.
(g) Atom-lattice with supraconductivity. Example, Pb.

According to the theory of structure presented in Chapter XV, the modifications of silica partake of the qualities of classes (b), (c), and (d). The X-ray results alone would place high-quartz and high-cristobalite in class (d), characterized by the fact that the lattice points are occupied by neutral atoms, each with its normal complement of electrons. Some facts, on the other hand, suggest the ion-lattice, (c).

In one respect the X-ray results and the electron theory of valence and chemical combination stand well together, for the known structures of high-

[3] Friederich, E., Zeitschr. f. Physik (1925) **31**: 813-826.

quartz and high-cristobalite are of exactly the type predicted by Huggins [4] from considerations of atomic structure, as developed by Kossel, Lewis, Langmuir, and others. The actual structure deduced by Huggins is wrong (see p. 241), but that particular structure is not a necessary consequence of the general hypothesis.

According to Huggins' hypothesis both the silicon and the oxygen atoms are surrounded by complete octets of electrons arranged as 4 pairs at

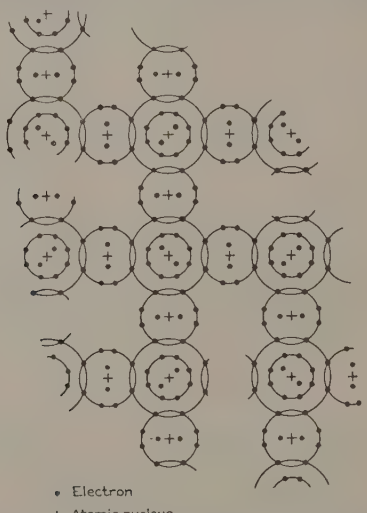


FIG. XVII.1.—Diagram to illustrate the grouping and sharing of electrons in the continuous primary-valence bonding characteristic of the structure of low-quartz, as proposed by Huggins. The figure shows the electron bonding but not the arrangement in space. Concentric double circles represent silicon, single circles represent oxygen, and + represents the atomic nucleus.

tetrahedral corners. Every silicon atom shares 2 electrons (1 pair) with each of 4 oxygen atoms, and every oxygen atom shares 1 pair of electrons with each of 2 silicon atoms. Every silicon atom is thus bonded to 4 oxygen atoms, placed at the corners of a tetrahedron. Every oxygen atom is bonded to 2 silicon atoms, also at two of the corners of a tetrahedron; but in this case the tetrahedron cannot be assumed to be equilateral because the other two corners are occupied by "lone pairs" of electrons which are not serving as bonds.

The bonding (but not the arrangement in space) I have represented in Figure XVII.1. This arrangement of four oxygens about each silicon and of an oxygen between each two nearest silicons is actually found in

[4] Article cited in XIV, note [16].

both high-quartz and high-cristobalite. But it cannot persist in the low-modifications, of whose existence Huggins' hypothesis takes no account.

Other types of electron bonding have already been discussed in Chapters III and XV.

Development of the theory of the high-low inversions

Theories of the structure of the principal forms of silica are necessarily closely tied up with theories of polymorphism, and particularly of the high-low inversions. These must next be reviewed.

The hypothesis that the high-low inversion of quartz is due simply to

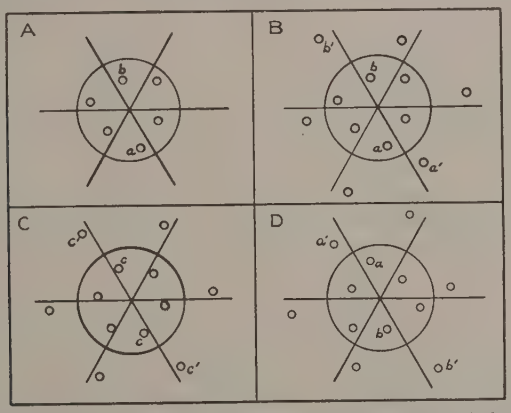


Fig. XVII.2.—Diagram to illustrate the change of symmetry and the possibility of twinning at the high-low inversion of quartz. After Mügge.

a change of shape of an atom-group, rather than to a change in the manner of the arrangement of the groups, suggested itself naturally to the first investigators of the inversion, Mallard and Le Chatelier. They did not attempt to define what that atom-group is, except to say that it is an "elementary crystalline particle" which is quasi-hexagonal or quasi-ternary, although in reality orthorhombic, monoclinic, or even triclinic. The inversion would then consist in a change in the symmetry of this "crystalline particle" from triclinic to monoclinic, or from monoclinic to orthorhombic, the symmetry of the mutual arrangement of the particles remaining unchanged.

Mügge [5] added to the definiteness of the hypothesis by suggesting that in low-quartz the smallest group of atoms possessing the symmetry of the crystal might be divisible into three sub-groups, each having monoclinic hemimorphous symmetry (see Table XII.1). Two directions in space serve to characterize such a unit. Suppose these pairs of directions (call them *a* and *b*) to be oriented as shown in the stereographic projection in Figure

[5] Article cited in VII, note [3].

XVII.2,A. Then the aggregate has trigonal trapezohedral symmetry, the symmetry of low-quartz. Now lying symmetrically with respect to the twofold axes of this aggregate are other corresponding directions, represented by a' and b' in part B. Suppose that at the inversion the sub-groups change their orientation in such a way that the directions a and a' take the same position, with respect to the one axial direction of the aggregate, as the directions b and b' take with respect to the opposite axial direction of the aggregate. The result will be a set of orthorhombic sphenoidal elements c, all similarly oriented, as shown in the projection, XVII.2, part C. The symmetry of the whole is now hexagonal trapezohedral, that of high-quartz.

On cooling, it is evident that the low-temperature structure can just as well become that shown in D as that in B. Suppose the one kind to begin at one point in the crystal and the other kind at some other point. As they spread from these two points they will finally come together along a surface which will be the composition-surface between the two individuals of a Dauphiné twin. This is simply a more concrete description of the effect described in general terms at p. 193.

Mügge further suggests that the directions a and b may represent a distribution of silicon and oxygen atoms, whose "chemical attraction" varies with the temperature.

The twinning-hypothesis of high-low polymorphism

Beckenkamp has been one of the most active exponents of the general theory of the existence of atomic and molecular groupings as the building units of crystals. According to his views, most crystalline substances do not exhibit the symmetry of any of their constituent atoms or even of their molecules, but only the symmetry of atomic or molecular groups of higher symmetry, such as is attained for instance by the assembling of molecules into enantiomorphous pairs. By the assumption of twinning on a molecular scale it is possible to explain the relations between the symmetries of polymorphous forms of a substance such as silica.

This twinning-hypothesis of the inversion of low-quartz to high-quartz is implied in Wietzel's deductions [6] from his data on heat capacity and latent heat. He says: "That twinned quartz shows a smaller heat of inversion is also to be expected, for twinning, which as is well known increases the crystal symmetry, represents a certain approach to the crystal-form stable above the inversion-point (here α-quartz), and will thus, furthermore, occur with an absorption of heat. Up to 575°, therefore, twinned quartz must have an energy content increased by the amount of this heat of twinning, as compared with ordinary quartz. Above 575° the two are not distinguishable from one another in crystal structure, and are evidently also not distinguishable in energy-content."

[6] Article cited in V, note [13].

If high-quartz and finely-twinned low-quartz are identical in structure and energy-content above 575°, they must have the same properties, the same melting-points, the same inversion-points into other modifications. Wietzel's argument falls into an inconsistency here, for he proceeds to calculate the "*A-U* diagrams" (curves of total-energy-change and usable-energy-change, see p. 356) for the two inversions, (1) quartz to cristobalite, and (2) finely-twinned quartz to cristobalite, and to assign two inversion-temperatures differing by about 200° C.

Wietzel [7] has himself recognized that the hypothesis as above stated leads into difficulties. He would emphasize only that twinned low-quartz *approaches* high-quartz in energy-content without becoming identical with it.

As we have seen, a given kind of twinning can not be invoked to explain a lowering of the melting-point of the high-modification and at the same time serve as an explanation of the mechanism of the inversion from low to high. This is not to say that a combination of two *different kinds* of twinning might not answer the requirements. However, no such hypothesis has yet been put forward.

The probable truth is that finely-twinned low-quartz inverts somewhere near 573° to finely-twinned high-quartz, which in turn will be in equilibrium with tridymite, or in metastable equilibrium with cristobalite, at a somewhat lower temperature than that at which untwinned quartz will be in equilibrium with those forms.

Wietzel,[8] on the basis of his heat-capacity data, has also ascribed the variation in the inversion-temperature of cristobalite to a difference in its degree of fineness or degree of twinning, or both combined. Fenner has already disposed of this hypothesis by experimental tests which have shown that the effect of fineness of grain or of variable twinning is too small to account for the large differences observed.

So far as quartz is concerned, the twinning hypothesis of high-low polymorphism does not match up with the structure of high-quartz as now known (Chap. XIII), and it will probably be no more successful with tridymite and cristobalite.

Niggli's hypothesis

Niggli [9] has explained the high-low inversion of quartz in terms of atomic positions, making the change from low-quartz to high consist wholly in a movement of oxygen atoms into positions of higher symmetry, such that the symmetry of the arrangement as a whole changes from trigonal to hexagonal. To this extent the hypothesis is in agreement with Beckenkamp's most recent structure (Fig. XIV.5), although Niggli's diagrams show too simple a pattern, since the silicon atoms are placed on the three-

[7] Correspondence with the author.

[8] Article cited.

[9] Niggli, P., *Lehrb. d. Mineralogie* (1920, Berlin) pp. 334-337; same, 2d ed. (1924, Berlin) Vol. 1: pp. 511-513.

fold axes. In the text of the second edition, however, it is recognized that this position is improbable.[10]

Smits' theory

Smits & Endell [11] have sought to apply Smits' theory of allotropy to the case of silica. Smits' theory is in essence an application of the Phase Rule to one-component systems under the basic assumption that any one-component system, especially one which shows phenomena of allotropy, is in fact a poly-component system in which the different components all have the same chemical composition, but exist as different "molecular species."

Having been found to work well for gaseous and liquid phases, particularly in the cases of sulfur and phosphorus, the conception was extended by Smits to the crystalline phases. The inner equilibrium between two or more molecular species in the liquid is supposed to persist in the crystal, making the crystalline phase in reality a solid solution of the two or more species. The relative proportion between the species is supposed to change with the temperature. A polymorphous change occurs when one of the component species reaches a point of saturation in the solid solution, forcing an "unmixing" and a shift to another solid solution of different composition and usually of different crystalline form.

As first applied to silica by Smits & Endell,[12] the hypothesis called for only two molecular species to explain the high-low inversions of quartz and cristobalite as well as the transformation of quartz into cristobalite. The further development of the theory by Smits soon showed that this hypothesis is quite inadequate and in the 1919 paper, already referred to, three species are assumed in internal equilibrium, two of which change promptly with changing temperature while the change of either of these into the third is assumed to be sluggish and capable of being held in unchanged proportion by chilling. These assumptions account for the inversion of quartz to cristobalite and for the high-low inversions of quartz and cristobalite, including the variation of the inversion-point of cristobalite with its previous history (see p. 126).[13]

No attempt was made in the earlier diagrams to include tridymite with its two high-low inversions. It is evident that this would greatly complicate the system if we were to extend the theory on the same basis as that described above. Additional molecular species would have to be introduced by hypothesis and the system would become too complex to be

[10] Since this Chapter was prepared, Niggli has published an excellent summary of the relations between structure and external morphology in quartz, in Zeitschr. Krist. (1926) **63**: 295-311.

[11] Smits, A., & Endell, K., *Notiz zu der Abhandlung über das System SiO_2*, Zeitschr. anorg. allg. Chem. (1919) **106**: 143-148.

[12] Smits, A., & Endell, K., *Über das System SiO_2*, Zeitschr. anorg. Chem. (1913) **80**: 176-184.

[13] The diagram and explanation of 1919 are used in the German (1921) edition of Smits' book on *Allotropy*.

represented completely by the usual binary or ternary diagram. In the 1922 English edition of Smits' book, however, the diagram has been modified to include the stability-range of high-tridymite in its proper relation

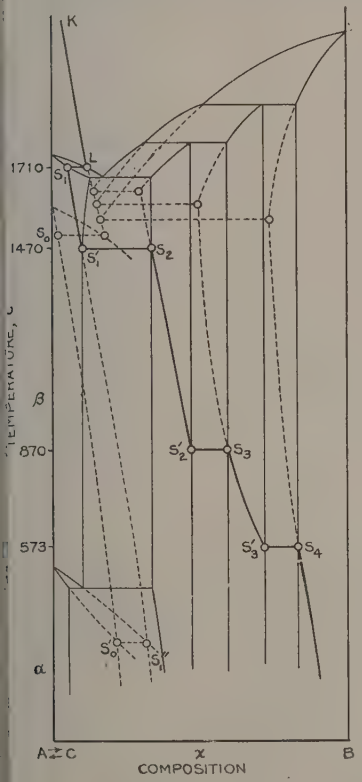


Fig. XVII.3.

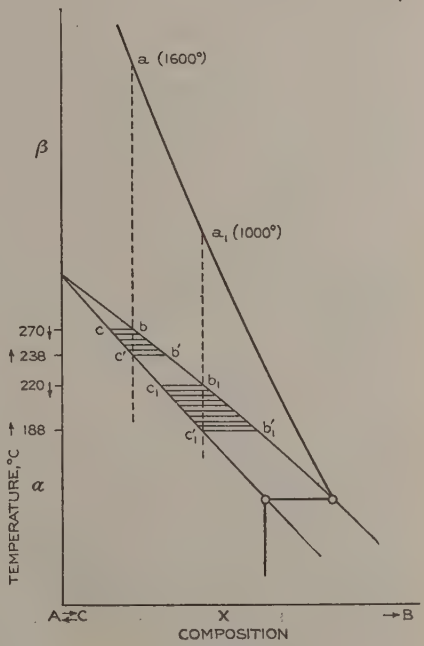


Fig. XVII.4.

Fig. XVII.3.—Diagram to elucidate the inversions of silica according to Smits' theory.

Fig. XVII.4.—Diagram to elucidate the variable high-low inversion point of cristobalite, on the basis of Smits' theory.

to cristobalite and quartz. This diagram is reproduced in Figure XVII.3, with a few temperatures corrected.

Smits' theory gives a very clear representation of the variability of the inversion point of cristobalite. This explanation is represented diagrammatically in Figure XVII.4. The composition of cristobalite made at 1600° is represented by the point *a*. If this cristobalite be cooled so

rapidly that no change occurs in the inner equilibrium, the change in composition with temperature will be represented by the vertical straight line *ab*. In the words of Smits: ". . . the transformation of β-mixed crystals into α-mixed crystals will commence at *b*. With the continued escape of heat this process proceeds further. During the displacement of the β-mixed crystal phase from *b* towards *b'*, theoretically the α-mixed crystal phase is displaced from *c* to *c'*, and when the α-mixed crystal phase has attained the latter composition the β-mixed crystal phase has just disappeared, having then all been converted into an α-mixed crystal phase *c'* of the same composition as the original β-mixed crystal phase. The transformation described here is of a *physical* nature only, and it has therefore taken place in the entire absence of internal change."

If, on the other hand, the cristobalite *a* is cooled from 1600° down to 1000° so slowly that the internal equilibrium between A-C and B follows the heavy curve to a_1, and is then chilled rapidly as before, the corresponding inversion phenomena are represented by b_1, c_1, b_1' and c_1', which come at a lower temperature, as Fenner found experimentally to be the case.

In the statement quoted above that "the transformation described here is of a *physical* nature only" we have specific recognition of a fundamental difference in character between the high-low inversions and the sluggish inversions, a difference not taken account of in the earlier stage of the development of Smits' theory as applied to silica.

The explanation as presented in Figure XVII.4 is still not complete, for it does not account for the facts that the inversion "overruns," that is, begins at a higher temperature on heating and at a lower temperature on cooling; and that this overrunning is a permanent and reproducible phenomenon for a given specimen of cristobalite. An explanation is readily provided, however, in the usual terminology of solid solutions, by supposing a certain amount of undercooling and superheating to occur in the hypothetical solid-solution phenomena represented by the area *bcb'c'*.

My only objection to Smits' theory is a general objection, already briefly stated at p. 244. It is that the theory fails to meet the crucial test of being able to predict facts or choices now unknown. The reason why it fails may be stated in the following terms. The theory is an application of the Phase Rule to a one-component system. The Phase Rule is a direct deduction from thermodynamics. Now thermodynamics is in effect a method of reasoning, and as such it does not introduce any fact, law, or hypothesis which did not already exist. Hence its conclusions, including any conclusions deducible from Smits' theory, are not different from the conclusions which could have been arrived at by some other path of reasoning which likewise introduced no new fact, law, or hypothesis.

If you have before you two alleged theories *A* and *B*, and if all the results of possible experiments or observations which you can deduce from *A* are indistinguishable from those which you can deduce from *B*, then

A and *B* are either meaningless or mean identically the same thing, no matter how different they may sound when said in words.

Smits' theory affords a convenient and useful means of representing graphically the polymorphism of silica, but it is not a real theory of the polymorphism of silica.

Perrier's hypotheses

With the radiational and electric properties of quartz particularly in mind, Perrier [14] has sketched the consequences of combining two hypotheses of structure, namely:

(1) The hypothesis of electric dissymmetry of the molecules; dipoles which are permanent or which are produced by displacement of bound electrons;

(2) The hypothesis of intermolecular actions which have the effect of a uniform electrostatic field proportional to the electric moment of the unit of volume; with introduction of the modifications brought about by thermal agitation of the molecules.

Underlying both of these hypotheses is of course the hypothesis of the existence of recognizable molecules in the crystal. The theory as a whole appears to be the electrical parallel of the Weiss theory of ferromagnetism.

Perrier has not applied the theory to questions of the stability and the interrelations of the principal forms of silica, but has made several applications of it to the properties of quartz, especially to the abrupt change in those properties at 573°.

It is a fundamental consequence of Perrier's two hypotheses, above, that there shall be a region of temperature where a mean orientation of the molecules persists, without the action of any external field; in other words, there is a spontaneous electric polarization of the molecules, corresponding to the "spontaneous magnetization" in ferromagnetism.

It is assumed that the elementary units of the crystals are polarized to saturation, and that the polarization varies with the temperature as a result of thermal agitation. With rising temperature the polarization decreases, finally disappearing at the inversion-point.

The discontinuity in properties at the inversion-point is explained by Perrier only in a very general way, as being analogous to the discontinuity in properties of a liquid at its boiling-point as explained by the theory of van der Waals.

The hysteresis in the properties at the inversion-point of quartz is explained as analogous to the overheating or undercooling shown by a liquid at its boiling or condensation temperature, corresponding mathematically to the overrunning of the formula of van der Waals. This means that the hysteresis should vary with the speed of heating or cooling, and that it should be possible, with suitable conditions of equilibrium, to wipe it out altogether. Here the theory is either not supported by

[14] Article cited in VII, note [10].

facts, or is in direct contradiction to facts. There is as yet no evidence that the temperature-hysteresis is dependent upon rate of heating and cooling in quartz and tridymite, and in cristobalite Fenner has shown definitely that it is independent of the rate (see p. 132).

The further consideration of these hypotheses will be postponed to the chapters dealing with radiational and electric properties.

Perrier's theory is similar in form to a more general theory due to Schrödinger. Schrödinger predicts the disappearance of the spontaneous polarization at the melting-point, the electrical forces being considered responsible for the resistance to deformation of the solid. Perrier, however (though apparently more by analogy than by direct analysis), predicts the disappearance of the polarization not at the melting-point, but at the inversion-point from low- to high-quartz, and this is in accord with the facts on piezo-electricity.

Hypotheses concerning the structure of micro-crystalline silica

The hypotheses of Washburn & Navias[15] on the constitution and structure of chalcedony and its changes when heated are partly in agreement with the theory as set forth in Chapter XVI and partly in contradiction to it.

Their hypothesis as to chalcedony and flint is: "Flint and chalcedony consist of colloidal quartz. In the purer forms of chalcedony the colloid is of the gel type and the individual colloid particles are microscopic or submicroscopic in size."

Here the stress is laid all on small *size*. I believe *shape* to be as important as size and perhaps more important. This is expressed in the hypothesis that *fibers* having a quartz structure are an essential part of the mineral. I should agree with them that smallness of dimension in the quartz units is essential, but the further assumption that these units are small in every dimension is not necessary.

Evidence that Fenner's chalcedony specimens do not consist of quartz fibers alone is found in the results of heating them with sodium tungstate at 750 to 850°. Quartz, being within its stability range, is not affected by such treatment. But chalcedony was found to yield new crystals of quartz, and in some experiments considerable *tridymite*. Now these are the products obtained by heating amorphous silica with sodium tungstate at 750 to 850°, and the natural deduction is that the chalcedony contained some amorphous silica.

Washburn & Navias explain the appearance of new quartz and tridymite in the above-mentioned experiments as follows: their "colloidal" quartz is unstable with respect to mega-crystalline quartz (see IX). Hence the colloidal quartz dissolves in the tungstate to form a solution saturated with respect to mega-quartz. From this solution are formed new crystals

[15] Article cited in XIII, note [24].

of quartz and tridymite as a kind of side-reaction, the main reaction being the deposition of silica on the larger quartz crystals already existing.

But, as Fenner [16] points out, this would require that the colloidal quartz should have not only a higher zeta (see XIX) than mega-quartz, as it is known to have, but also a higher zeta than mega-tridymite at the same temperature, which seems improbable, because the difference in zeta between fine and coarse crystals of a given modification is usually of a smaller order of magnitude than the difference in zeta between two different modifications.

On the other hand, this argument assumes that the appearance of tridymite is subject to the laws of stable and metastable equilibrium. But silica has a way of assuming evanescent and temporary forms, and we might imagine that this is what is happening in this case. Once in solution, it might by a local heaping up of energy separate out in the tridymite form.[17] This hypothesis will serve to explain the appearance of tridymite provided the crystallization of that form is quite independent of the original source of the silica, that is, if silica dissolving in sodium tungstate does not carry into solution enough inherited structure to influence its recrystallization. This is a question which could be tested by experiment.

Washburn & Navias, in attempting to explain the abnormally low density and refractive index of the cristobalite produced from chalcedony, and again Washburn,[18] in replying to Fenner's discussion of their paper, have introduced the rather radical hypothesis that a continuous gradation is possible from a perfect quartz or cristobalite structure through more or less distorted patterns into a completely amorphous structure. The hypothesis is stated thus: "There must be a gradual gradation of properties extending all the way from those of isotropic silica glass on the one hand up to macro-crystalline cristobalite on the other, depending upon the degree of dispersion. . . . A crystal composed of a comparatively small number of molecules, especially if not well formed, must be more or less distorted by forces of the nature of surface tension and corresponding changes in its refractive index are to be expected."

There is little experimental support for such a supposition. Most of the X-ray evidence is to the effect that a substance is either definitely and almost perfectly crystalline, or it is not crystalline at all; if any distortion of the structure is possible it is relatively small in amount. This is in agreement with the fact, known from experiments on compressibility and elasticity, that the interatomic forces in a crystal oppose a very large resistance to any general distortion.

On the other hand it must be remembered that most of our knowledge of the structure of crystals concerns the kind of substances upon which most physical and chemical work has been done, namely, salts, metals, and

[16] Bull. Amer. Ceram. Soc. (1922) **1**: 298-300.
[17] Dr. Fenner does not believe this to be an allowable explanation.
[18] Bull. Amer. Ceram. Soc. (1922) **1**: 300-301.

organic compounds. But silica is so sluggish in its movements and apparently so easy to freeze into almost any sort of arrangement which it happens temporarily to possess, that Washburn's hypothesis deserves to be considered. I have already used it cautiously and in a much milder form at p. 259.

Other hypotheses concerning the sluggish inversions

Devitrification

Washburn & Navias [19] propose the hypotheses (a) that a rearrangement of silica into cristobalite groupings begins throughout the mass of a fragment of vitreous silica heated to devitrifying temperatures; and (b) that the initial result of this rearrangement is the production of a large number of "colloidal" cristobalite crystals immersed in glass. From this second hypothesis they deduce that vitreous silica heated at 1400 to 1500° should yield a product similar to the product of low density obtained by heating chalcedony at similar temperatures.

Their hypothesis (a) is the same as that offered at p. 255, but with (b) the facts are not in agreement. In the first place, the cristobalite crystals form most rapidly at the free surfaces and grow inward; and, secondly, the cristobalite formed from vitreous silica always has nearly the normal density, while that from chalcedony is 4 to 6 per cent low.

Speed of transformation

Mellor & Campbell [20] have pointed out that the speed of transformation of quartz into cristobalite indicates a reaction of the unimolecular type. The speed of such a reaction does not depend on the coming together of two or more units, and the rate of change at any moment depends simply on the amount left unchanged at that moment. Expressed in symbols: $dx/dZ = -Kx$, in which x is the fraction of the total which remains unchanged, Z is the time, and K is a constant for this reaction at this temperature. If the equation is integrated, and the time Z is measured from the beginning of the reaction, when $x = 1$, then $x = e^{-KZ}$, that is, the curve of change is logarithmic.

The authors therefore suggest the following chemical equation to represent the transformation of quartz into cristobalite: $(SiO_2)_{n+m} \rightarrow n(SiO_2)_m$. But, as they themselves remark, the logarithmic curve does not by any means prove that the suggested reaction is the only one possible. The logarithmic curve accords equally well with the set of hypotheses presented in Chapter XV.

[19] Article cited in XIII, note [24].
[20] Article cited in V, note [17].

New features of the theory of Chapter XV

In the foregoing notes I have attempted to indicate, although very incompletely, how the general theory of the structure of silica presented in Chapter XV has developed from numerous partial hypotheses, and also how it compares with other hypotheses which are under discussion at the present day. My own contributions to the theory are essentially four:

(1) The hypothesis of the polymorphous high-low inversions, according to which they are due to the passage of a moving mechanism through a stage of mechanical instability.
(2) The hypothesis of an incompletely crystalline structure for cristobalite to explain its variable inversion-point and various other phenomena.
(3) The hypothesis of two types of structure in vitreous silica and the silicate glasses.
(4) The general synthesis of existing hypotheses into a theory applicable to all the modifications of silica.

I had supposed, when first attempting to assemble the various hypotheses into a consistent theory (1922), that the "thread hypothesis" for the forms of silica, stated in XV (E), was also new, but found later that it had already been proposed by Wallerant,[21] although little attention seems to have been paid to his suggestion. This same hypothesis was independently adopted by W. H. & W. L. Bragg [22] in explaining the structure of quartz (see XIV), but has been subsequently abandoned by them.

[21] Wallerant, F., Bull. Soc. Franc. Min. (1897) **20**: 52-100.
[22] *X-rays and crystal structure*, 4th ed. (1924).

Chapter XVIII. THE DENSITY OF SILICA

Density and specific volume

That property of matter which appeals earliest and oftenest to our senses is its quality of occupying space, or of possessing dimensions as well as inertia and weight. The space occupied by a given mass (its *volume*) or the mass of a given volume of the substance (its *density*) are thus characteristic and mutually dependent constants of the substance.

In the customary c.g.s. units, the *specific volume* of a substance is defined as the *volume in cubic centimeters occupied by a mass of 1 gram* of it. Its *density* is defined as the *mass in grams of 1 cubic centimeter*. The one constant is thus the mathematical reciprocal of the other, and they may be used interchangeably. The usual symbols are: specific volume, v; density, d.

The term "specific gravity" is used rather loosely. It will be defined for present use as the ratio of the mass of a given volume of the substance to the mass of the same volume of pure water, the water being at the same temperature as the substance or at some other specified temperature. It would be a superfluous constant were it not for the fact that density is nearly always determined by weighing in water. The primary result of this measurement is a specific gravity value, which can then be converted into true density only with a knowledge of the density of water. This latter constant is known to a high precision, but not higher than the precision with which a value of specific gravity can be determined. Hence some prefer to report results of such measurements only as "specific gravity" without taking the additional step of converting them to true density. For example, the word "Dichte" (density) is not found in the Landolt-Börnstein-Roth-Scheel *Tabellen* of 1923.

Specific gravity will not be employed in this book, except in discussing experimental precision or in quoting authors who have determined a so-called "specific gravity" without recording the temperature of the water which they took as the standard. Such data cannot be used where accurate values or precise comparisons are called for, but in many cases more precise data are entirely lacking.

The specific volume of most substances is less than 1. To avoid the use of decimals it is sometimes convenient to use 1000 v instead of v, calling it the *kilovolume*, that is, the *volume of 1 kilogram in cubic centimeters.*

Density and specific volume of the forms of silica

The best values for the densities and kilovolumes of the modifications of silica at atmospheric pressure and 0°C are given in Table XVIII.1. The accuracy of the basic data is not high enough to justify giving separate values for room temperature except in the case of quartz, for which d at 20° is 2.649 and 1000 v is 377.5.

The density of some specimens of cristobalite, made from very fine-grained micro-forms of silica, is considerably lower than the value given in the table, and may be as low as 2.20. This difference is probably real, and not due merely to fineness of grain whereby the pyknometer liquid is prevented from penetrating submicroscopic pore spaces.

TABLE XVIII.1.
DENSITY AND KILOVOLUME OF SILICA AT 0°C AND 1 ATMOSPHERE.

Modification	Density	Kilovolume
Low-quartz	2.651	377.3
Low-tridymite	2.26	442.
Low-cristobalite	2.32	431.
Vitreous silica	2.203	453.9

CONSTANCY OF THE DENSITIES

Quartz

A great many measurements have been made of the density of quartz with specimens from all quarters of the Earth. An examination of the data should show to what degree the density is an unchanging and reproducible property of the substance.

After throwing out all observations which are of low precision or which have been made under undefined conditions, it is possible to conclude from the remainder that:

(A) The density of all the clear transparent quartz which has been carefully examined lies within the limits 2.648 and 2.650 at room temperatures.

(B) There are real differences in the densities of specimens of clear transparent quartz. These differences do not exceed 0.0005 or about 0.02 per cent, and are probably less than this amount, but are not less than 0.0001 or about 0.004 per cent.

From the discussion which follows it will be evident that there is no longer any excuse for measuring the density of a specimen of quartz with a precision poorer than 0.1 per cent. It can be taken from a table of physical constants with greater certainty. The density at 20° of all clear transparent quartz on the Earth's surface may be conservatively stated, "without fear of successful contradiction," as 2.649 ± 0.002.

The effect of fine subdivision on the density, if there is any effect at all, is not more than $\pm$ 0.03 per cent.

Vitreous silica

The density of average specimens of clear vitreous silica is less constant from specimen to specimen than is the density of quartz. Differences of 0.05 per cent are known to exist in vitreous silica, and differences as large as 0.1 per cent are likely to be found. The differences are probably real,

although there has been no rigid experimental proof that they are not due to small amounts of impurities fused with the silica.

General remarks on the constancy of the properties of quartz

Any discussion of the constancy of the properties of quartz ultimately simmers down to the question, what constitutes perfection in a quartz crystal? We recognize at once that the commonly occurring white vein quartz, whose whiteness is due to the inclusion of many very small bubbles, may not be expected to be constant in density from specimen to specimen, nor to agree in density with transparent quartz. But even quartz which seems perfectly clear and transparent and bounded by perfect faces, as viewed by the unaided eye, may vary in quality. Its commonest fault is twinning, the juxtaposition of two or more individual crystals differently oriented, although the boundaries between them may be quite invisible. The crystal may contain minute inclusions, visible only under the microscope. It may be faintly colored with an impurity which is wholly invisible under the microscope. All such variations may reasonably be expected to be accompanied by small variations in the numerical value of any physical property, such as density, index of refraction, or electrical conductivity.

Any judgment as to the constancy of a given property of quartz must then be accompanied by some statement as to the tests for quality to which the specimens have been subjected.

Since clear transparent quartz crystals are prized for optical instruments, the most common test for quality is the examination in polarized light applied by the makers of such instruments (see p. 835). This reveals twinning and other flaws. Crystals which have passed such a test have usually been considered as equally perfect, and suitable subjects for a study of the constancy of properties.

More searching tests can be used, however, (see p. 835) such as the method of striae, the method of rotatory compensation, or the special test used by Lowry in connection with his study of the rotatory power (see XXXIII). 10 out of 12 cylinders of quartz, previously considered perfect, were shown by Lowry's tests to possess slight flaws, which had a determinable effect on the measurements of rotatory power.

Optical quartz must then be classified as of two kinds: (1) that which will pass the most searching optical tests, and (2) that which will not pass such tests. Practically all of the quartz on which studies of constancy of properties have been made is of unknown quality as between these two classes.

It is important to note, however, that the flaws discovered by Lowry are due entirely to twinning.[1] Such flaws might conceivably have an easily measurable effect on optical properties, particularly rotatory power, and yet be without any measurable effect on density.

[1] Personal communication by correspondence with Dr. Lowry.

Nevertheless, in the absence of definite information on the relation between optical flaws and variations of density, we can only say conservatively that differences of the order of magnitude found by Lowry in rotatory power, namely, about 0.01 per cent, may be expected to occur, and may not be taken as proof that the density or other property in question is actually inconstant to that degree.

The experimental data on the density of quartz

It is easily possible to determine the density of quartz with an accuracy of 0.05 per cent, equivalent to about 0.0013 in the actual value. In comparing different specimens under the same conditions it is also easily practicable to get a precision of 0.01 per cent or about 0.0003 in the actual value.

At atmospheric temperatures the specific volume of quartz changes by about 0.0035 per cent per degree or about 0.0001 in the actual value. In precise measurements the temperature should therefore be known within 1°.

From the foregoing it is evident that determinations with a precision poorer than ½ per cent (0.01 in 2.65) are not worth considering at all. The same is true of all determinations in which the author, as is all too commonly the case, reports "specific gravity" without telling the temperature of the water with which the substance is compared, for the difference between the true density and the specific gravity referred to water at 25° is 0.008 in 2.650. So loosely are words used by scientists that even if the author gives a figure as "density" it cannot be assumed to be true density unless there is a definite statement or some numerical evidence to prove it.

A correction which is sometimes overlooked is the reduction of weighings in air to true weights, by allowing for the buoyancy of the air. The apparent density of quartz, determined by weighing in air and in water without the buoyancy correction, is 0.0020 greater than the true density.

Measurements on the Paris standards

Probably the most accurate absolute measurements ever made of the density of any substance are the measurements by Macé de Lépinay, Buisson, & Benoit on quartz. These form part of a series by several investigators, made about 1905 to 1910 at the International Bureau of Weights and Measures, and designed to determine the exact relation between the cubic decimeter and the liter.

The measurements in question were made on two cubes of quartz, selected for high optical quality and cut as perfect geometrically as the optician's art made possible. One cube was 4 cm on an edge, the other, 5 cm. They are designated as C_4 and C_5, respectively. The absolute specific volume of each was determined by measuring (1) its mass in terms of the standard kilogram and (2) its linear dimensions in terms of the standard meter through the

intermediate use of the wave-length of cadmium red light, which has been compared with the standard meter by Michelson and Benoit.

The first set of measurements on one of these cubes (C_4) was published by Macé de Lépinay in 1895-1897. The principle adopted as the basis of the measurement of dimensions of the cube was that of "Talbot's bands," which are seen in the spectrum when half of the beam of light entering the spectroscope passes through the plate to be measured while the other half passes through the air only. The evaluation of the results requires that the index of refraction be known accurately, and this was measured by Macé de Lépinay on a prism cut from the same block (see p. 605).

It developed later that the constancy of the refractive index of quartz cannot be depended upon to the precision demanded in work on the fundamental standards of length and mass, and further measurements were undertaken by Fabry, Macé de Lépinay, & Perot [2] in which the index of the substance itself was eliminated by employing the method of interference between rays reflected from the surfaces of plane glass plates which were in contact with the faces of the cube but which projected beyond its edges.

TABLE XVIII.2.

DENSITY OF QUARTZ DETERMINED BY MEASUREMENTS OF THE DIMENSIONS AND THE MASSES OF CUBES.

Cube	Mean thickness: Faces	Mean thickness: Thickness μ	Volume at 0° cc	Mass grams	Density g per cc
C_4	2–5 1–6 3–4	39 052.270 39 774.298 38 557.191	59.889 981 *	158.748 444	2.650 668
C_4			59.890 030 †	158.748 444	2.650 666
C_5	1–6 2–5 3–4	49 487.72 49 678.17 49 894.89	122.664 56 *	325.131 123	2.650 571
Difference between C_4 and C_5					0.000 096

* Measured with cadmium red light.
† Measured with cadmium green light.

The final measurements, published jointly under the names of Macé de Lépinay, Buisson, & Benoit [3] in 1910, utilized the principle of solving two simultaneous equations containing both the index of refraction and the width of the cube. One equation comes from the interference of light reflected from the front and the rear face of the cube; the other equation comes from the interference between two rays of light one of which has passed through the cube while the other has passed through the air parallel to the path of the first ray. The development of interferometric methods and apparatus which had taken place since Macé de Lépinay first applied them to this problem permitted the measurement of the dimensions of the 4-cm and 5-cm cubes to a very high precision.

[2] FABRY, CH., MACÉ DE LÉPINAY, J., & PEROT, A., Compt. rend. Acad. Paris (1899) **128**: 1317-1319.

[3] MACÉ DE LÉPINAY, J., BUISSON, H., & BENOIT, J. R., *Determination du volume du kilogramme d'eau,* Trav. Mem. Bur. Int. Poids et Mesures (1910) **14**: 277 pp.

The variation of planeness of the faces was taken account of, and contour maps with intervals as small as 0.02 μ,—probably the smallest contour interval ever used on a map,—were made of the pairs of faces. The angular deviations from a perfect cube were also taken account of, and were found less than 4 seconds, too small to affect the volume appreciably. Dimensions were reduced to 0°C by means of linear expansion coefficients independently determined on each cube (see p. 372). The weighings to determine the mass could be, and were, made with even higher precision than the measurement of linear dimensions.

The summarized results, containing absolute values of the density which I have calculated from the published data,[4] are given in Table XVIII.2.

The second part of this research on the relation of the cubic decimeter to the liter consists in the measurement of the specific gravity of the quartz in terms of water at 4°C as unity, by weighing the cubes in water. The results were reduced to water at 4° by the data of Chappuis on the dilatation of water. The results thus obtained are:

Cube	Number of weighings		Temp. water	Sp. gr. at 0° (water at 4° = 1)
	In air	In water		
C_4	38	28	10.095 to 17.381°	2.650 739
C_5	21	22	11.061 to 12.182°	2.650 645
			Difference	0.000 094

The precision of these measurements is estimated as 0.000 002, so that there can be little doubt of the existence of a real difference between the values of the average density of the quartz in the two specimens, amounting to 0.000 096 or 0.000 094 according as the one or the other pair of figures is taken.

The agreement between the two differences, 96 and 94 millionths, is only another way of saying that the values of the true density of water at 4°, obtained with the two cubes, are in agreement to 0.000 001. The adopted value for this constant is 0.999 973.

The difference in density between the quartz cubes was found to be accompanied by differences, all in the same direction, in thermal dilatation, index of refraction, birefringence, and rotatory power. These will be considered in later chapters.

Other data on the density of quartz, obtained with national standards of mass

The work on the standard kilogram and meter at Paris, just described, is not the only work of this high grade which has been done on quartz. There are also available the following investigations: on the Austrian standards, by Steinheil (1837) and by Pierre (1867); on the Bavarian pound, by Steinheil & Seidel (1844); on the English pound, by Miller (1846); and on a standard quartz weight of the International Bureau, by Marek (1884).

It is rather surprising that these data on the density of quartz, including

[4] The authors use the word *densité* in the meaning of "specific gravity referred to water at 4°."

some of the best in existence, should never have found their way into the standard tables of physical and chemical constants.

Marek,[5] at the International Bureau, used a standard 400-gram spherical quartz weight (Q400) to determine the difference in density between pure water and water charged with air. 48 determinations, each consisting of 7 weighings, were made at temperatures of -0.2 to $+21.3°$, yielding as direct result the masses of volumes of water equal to the volumes occupied by Q400 at the various temperatures. Taking the density of water at 4° as standard, and the formula

$$V_t = V_0(1 + 32.936 \times 10^{-6}t + 37.15 \times 10^{-9}t^2)$$

for the dilatation of quartz over the range of 0 to 20°, the author calculated the specific gravity of both kinds of water in terms of water at 4°.

A by-product of this investigation is the specific gravity of quartz at 0° referred to pure water at 4°, for which the value 2.650 74 was obtained. The true density at 0° is therefore 2.650 67.

Miller's measurements[6] on the English secondary standard pound "Q", made of quartz in the form of a cube, were made in 1846. The source of the quartz and its optical quality are not recorded. The result of 6 sets of determinations, at temperatures of 17.3 to 17.65° by a standard Kew thermometer, yield an average specific gravity at 18° referred to water at 18°, of 2.652 590. The true density at 18° is therefore 2.648 863 and at 0°, if the dilatation is the same as that of Benoit's specimen, 2.650 495.

The earliest measurements of this class were those of Steinheil,[7] who in 1837 compared the standard quartz kilogram B^k, made of Brazilian quartz, and later owned by the Kingdom of Naples, with the original kilogram at Paris. 9 sets of weighings were made in air and water at temperatures in the neighborhood of 17° and 24°, from which both the specific gravity and the dilatation were obtained.

More exact values for the density of air and of water having become available since Steinheil's time, his data were recalculated in 1870 by Herr,[8] who used new tables for air and water, but retained the principle of determining the dilatation and density of quartz simultaneously. This is not a very reliable method for the dilatation, depending so much as it does on an exact knowledge of the dilatation of water, and the results as reduced to 0° magnify the uncertainty in the dilatation of quartz. A better result for comparison, therefore, is obtained by using more recent dilatation data on quartz, determined on other specimens, but much more reliable than those of Steinheil.

I have made this recalculation, depending upon Herr for the air corrections, but using Thiesen, Scheel, & Diesselhorst's specific gravities for water and Benoit's dilatation curve for quartz. The results of Steinheil's measurements, grouped into two groups, are then:

[5] Marek, W. J., *Pesées exécutées au Bureau International,* etc., Trav. Mem. Bur. Int. Poids et Mesures (1884) **3**: D, 142 + 116 pp.

[6] Miller, W. H., Phil. Trans. Roy. Soc. London (1856) **146**: pp. 894-903.

[7] Steinheil, C. A., *Ueber das Bergkrystall-Kilogramm, auf welchem die Feststellung des bayerischen Pfundes . . . . beruht,* Abhandl. K. Bayer. Akad. Wiss., Math.-Phys. Cl. (1844) **4**: Abt. 1, 163-244.

[8] Herr, J., and others, *Ueber das Verhältniss des Bergkrystallkilogrammes . . . zum Kilogramme der Kaiserlichen Archive,* etc., Commissions-Bericht, K. K. Handels-Ministerium, Wien (1870), 136 pp.

Temp. of measurement	d at 0°
16.78°	2.650 566
23.89°	2.650 310

The Austrian standard kilogram $\odot^k$, made of Swiss quartz, was compared by Steinheil with B^k in 1846. One of the duties of Herr's Commission was the revaluation of this important comparison, and incidentally to this work the density of $\odot^k$ was measured for the first time by V. Pierre.[9] I have recalculated the results to the same basis as B^k above, with the following result, derived from 5 weighings at about 11°C: True density at 0° = 2.650 732.

Steinheil & Seidel[10] measured the specific gravity of the Bavarian "Normalpfund," made of quartz from Madagascar, in air-free water at 9.5 to 10°C. Five determinations gave the mean value 2.650 924 ± 0.000 005, using Bessel's table for the dilatation of water, and the value 10.8×10^{-6} for the mean linear expansion of quartz. The value 2.650 962 ± 5 was obtained in water saturated with air. Recalculation with modern data on water and quartz, as above for B^k and $\odot^k$, yields 2.650 756.

The foregoing determinations are summarized in Table XVIII.3, recalculated to a common basis, namely, true density at 0°, and rounded off to five decimals. The measurements by Steinheil on B^k are probably less reliable than the others, because, as already noted by Herr,[11] his temperatures were not as constant as they should have been for work of this grade.

TABLE XVIII.3.

COMPARISON OF DENSITY DETERMINATIONS ON QUARTZ STANDARDS OF MASS.

Investigator	Quantities measured	Source of quartz	True d at 0° g per cc
Macé de Lépinay, Buisson, & Benoit	Dimensions and linear expansion of 2 cubes		2.650 67 2.650 57
Marek	Wt. 400-gram sphere in water		2.650 67
Pierre	Wt. of Kilogram ⊙ in water	Switzerland	2.650 73
Steinheil	Wt. of Kilogram B^k in water	Brazil	2.650 44
Steinheil & Seidel	Wt. of Bavarian Pfund in water	Madagascar	2.650 76
Miller	Wt. of pound cube in water		2.650 50
		Mean	2.650 62

[9] HERR & others, Report just cited, pp. 54-57.

[10] STEINHEIL, C. A. & SEIDEL, Letter to Schumacher, 29 March, 1844, publ. in *Briefwechsel zwischen Gauss und Schumacher* (Altona, 1862), Vol. 4: pp. 235-238.

[11] HERR & others, p. 25 of report cited.

Other data of precision on the density of quartz

In addition to the foregoing measurements on the standards of mass, measurements of equally high precision on the density of quartz have been made by Macé de Lépinay (1886), and Warrington (1899); and of somewhat lower precision by Berkeley (1907), Stierlin (1907), Sosman (1911), Madelung & Fuchs (1921) and Ahlers (1924). With this set should also be included Johnston & Adams' (1912) value of 2.6483 at 25°, which will be discussed at p. 299. Direct comparisons of the densities of various specimens have been made by Merwin (1911) and Ahlers (1924).

Macé de Lépinay[12] found the specific gravity of a 13-gram crystal from Brazil, referred to water at 4°, to be 2.650 85, when calculated to a temperature of 0° with a preliminary dilatation coefficient. As the original data are not given, this cannot be recalculated with Benoit's coefficients, but the difference is in the sixth place and therefore inappreciable.

A precise determination of the specific gravity of quartz referred to water at 4° was made by Warrington[13] in testing a newly devised "hydrometer of total immersion." The mean of 5 measurements on a 32-gram crystal is 2.648 235 ± 0.000 032 at the mean temperature 24.355°.

The Earl of Berkeley[14] made a series of careful determinations of the density of powdered ignited quartz using a conical pyknometer with ground-in thermometer. While this form of pyknometer gives the temperature directly it is not as accurate as Johnston & Adams' form (see p. 299) because of the possibility of variations in volume in successive replacements of the thermometer. Water and carbon bisulfide were used as immersion liquids. The results are:

Liquid	No. of determinations	Temp. range	Density at 21°
Water	5	21.24 to 21.95	2.6487 ± 0.0001
CS_2	6	18.24 to 21.14	2.6483 ± 0.0002

Stierlin[15] measured the density at 16.8° of a 10-gram crystal by duplicate weighings in water and air, and obtained the values (recalculated to true density):

	2.649 47
	2.649 52
Mean	2.649 50

My own measurements[16] were made by weighing in air and water, in connection with experiments on the volume-change of rocks upon fusion, and were on pebbles of clear quartz from Minas Geraes, Brazil. The results are:

[12] Macé de Lépinay, J., Journ. de Physique (1886) (2) **5**: 411-416.
[13] Warrington, A. W., Phil. Mag. (1899) **48**: 498-519.
[14] Berkeley, *On the more exact determination of the densities of crystals*, J. Chem. Soc. London (1907) **91**: 56-62.
[15] Stierlin, H., *Einige physikalische Eigenschaften des gegossenen Quarzes*, Vierteljahrsschr. Naturf. Ges. Zürich (1907) **52**: 382-418.
[16] Sosman, R. B., Unpublished data, Geophysical Laboratory.

Wt. of specimen grams	Temp.	*d*	
44	20.5	2.6490	As received
Same	19.2	2.6493	After heating to 550°
34	19.5	2.6491	As received
35	20.2	2.6489	As received
40	20.5	2.6492	As received
Mean	20.0	2.6491	

Madelung & Fuchs [17] measured the volume at 0° of 4 specimens of quartz by displacement of mercury, in connection with measurements of compressibility. Their results, in specific gravity [18] referred to water at 4°, are:

8.5 gram crystal from Madagascar	2.6497
8.5 gram crystal from Striegau	2.6493
10.5 gram crystal, source unknown	2.6486
10.3 gram crystal, source unknown	2.6495

Merwin [19] compared the densities of 12 specimens of quartz from various localities by immersion in Thoulet's solution. All but two were alike in density; one of these, from Herkimer County, New York, sank slowly, the other (origin unknown) rose. Their deviations from the others were shown by a Westphal balance to be of the order of 0.0003. The true density of the ten was near 2.6493 at 20°, as shown by my independent determination on one of the large specimens (see above).

Ahlers [20] likewise determined the relative specific gravity of 12 specimens of quartz by suspension in Thoulet's solution, measuring the density of the solution with a Westphal balance. The balance was not directly calibrated at densities greater than unity. The first 11 specimens ranged in weight from 3 to 814 mg., while the last was a sphere weighing 88 grams. All were clear and free from microscopic inclusions or cracks.

The difference between highest and lowest is 0.0004. As the sensitivity is about 0.0002, the results may be taken to establish the constancy of density of these 12 specimens within about 0.0003, which is the amount of deviation found by Merwin.

Ahlers also made 10 determinations of the density of the 88-gram sphere referred to above, by weighing in air and in water of temperature 13 to 16°. The results, calculated to 0° and referred to water at 4° as unity, average 2.6505 ± 0.0001.

All but one of the independent determinations discussed in the foregoing pages are assembled for comparison in Table XVIII.4, after reduction with the aid of Benoit's coefficients to the common basis of true density at 0°C. The mean is confirmatory of that in Table XVIII.3.

[17] Madelung, E., & Fuchs, R., Ann. Physik (1921) **65**: p. 307.
[18] According to correspondence with the author.
[19] Merwin, H. E., *Quartz and fluorite as standards of density and refractive index*, Amer. J. Sci. (1911) **32**: 429-432.
[20] Ahlers, L., *Über die Dichte von Quarz*, etc., Zeitschr. Krist. (1924) **59**: 293-334.

TABLE XVIII.4.

COMPARISON OF HIGH-GRADE DETERMINATIONS OF THE DENSITY OF QUARTZ, OTHER THAN THOSE ON STANDARDS OF MASS.

Investigator	True d at 0°
Macé de Lépinay	2.650 78
Warrington	2.650 39
Berkeley	2.650 4
Stierlin	2.651 0
Sosman	2.650 9
Johnston & Adams	2.650 5
Ahlers	2.650 4
Mean	2.650 6

TABLE XVIII.5.

JOHNSTON & ADAMS' MEASUREMENTS ON THE DENSITY OF FINELY CRUSHED QUARTZ.

Values are specific gravity at 25° referred to water at 4°.

Fraction	d	Mean d	Pyknometer
Through 40, on 60 mesh-per-inch sieve	2.6487 2.6455 2.6456 2.6471 2.6466 2.6472	2.6468	Old type
Same	2.6471 2.6469	2.6470	New type
Through 80, on 100 mesh-per-inch sieve	2.6478 2.6476	2.6477	New type
Through 100, on 120 mesh-per-inch sieve	2.6466		Old type
Through 200 mesh-per-inch sieve	2.6492 2.6481 2.6468 2.6471 2.6485 2.6495 2.6483 2.6463	2.6480	Old type
Same	2.6488 2.6477 2.6483 2.6481	2.6482	New type
Particles suspended in water, first fraction	2.6492 2.6486	2.6489	New type
Particles suspended in water, second (residual) fraction	2.6483 2.6477	2.6480	New type

The determinations of Madelung & Fuchs are omitted from Table XVIII.4. The mean of their determinations, made directly at 0°, is 2.6493, which is appreciably (0.04 per cent) lower than the others. The suspicion can not be avoided that the mercury, with its high surface tension and its failure to wet the surface, left some small unoccupied corners or failed to fit the surface closely at all points, thus making the volume appear too large.

Supposed effect of fine subdivision on the density of quartz

Johnston & Adams[21] sought to find out whether very fine subdivision changes the density of quartz. They used the finely crushed crystalline quartz employed in the Geophysical Laboratory for silicate syntheses and separated it into various fractions, making 27 measurements, with two types of pyknometer. One type was the familiar bottle pyknometer with ground beveled stopper, the other a new type of bottle pyknometer with a flat polished stopper, a form which gives higher precision. The fractions were dried at 200° for ½ hour. Special tests showed that the density of even the finest material was not appreciably affected by exposure to the air for 48 hours. The detailed results are given in Table XVIII.5.

The results are summarized in Table XVIII.6. I have estimated the dimensions of the particles in the sifted fractions from the standard diameters of opening of the series of sieves. The diameters of the last two fractions (separated by sedimentation of the 200-mesh material) were measured under the microscope.

Table XVIII.6.

Summary of Johnston & Adams' Results on Density of Finely Crushed Quartz.

Diameter of grains mm	d at 25°
0.2 to 0.4	2.6469
0.14 to 0.17	2.6477
0.12 to 0.14	2.6466
0.07 and smaller	2.6481
0.05	2.6489
0.02 down to limit of vision	2.6480

The results seemed at first to indicate an *increase* of density toward the finer material. Optical examination of the fractions showed, however, that although a preliminary sample had been optically satisfactory, the sample used for the tests contained some microscopic bubbles and inclusions in the larger fragments. The particles of 0.05 mm diameter were found to be clear. Evidently the slight increase in density was due to the opening up of the bubbles, and the values found for the coarser particles are therefore slightly lower than the true density. It can be said with fair certainty, then, that there is

[21] Johnston, J., & Adams, L. H., J. Amer. Chem. Soc. (1912) **34**: p. 571.

neither a decrease nor an increase of density of more than 0.03 per cent with subdivision.

Ray[22] recently published the results of some experiments which he interpreted as showing that a large proportion of a specimen of quartz which is subjected to long-continued grinding is rendered amorphous thereby. "Silver sand" was ground in the dry state[23] for 15 hours in a mechanically operated agate mortar. A sample of the product was dried at 150°C, and its density was determined in a 10-cc pyknometer with redistilled carbon tetrachloride as displacement liquid. The results were as follows:

	d at 16-17.6°	
Silver sand, unground	2.638 2.640 2.637	2.638
Silver sand, ground 15 hr	2.530 2.526 2.528	2.528
Vitreous silica, crushed	2.208 2.206 2.210	2.208

These results indicate the conversion of about 26 per cent of the sand into amorphous silica. Paralleling this test is Ray's determination of the heat of solution of the finely ground sand in hydrofluoric acid (see p. 323) which indicates that about 31 per cent has been rendered amorphous.

In view of Johnston & Adams' results, it is difficult to believe that dry grinding could cause so great a change, and I have therefore sought for optical confirmation of the result. An examination by H. E. Merwin of some quartz ground under water for 14 hours in a mechanical mill in an agate mortar showed that all the particles were still crystalline quartz, varying in size from 4 to 40 μ (0.004 to 0.04 mm). This material was further ground dry for 12 hours, and still consisted entirely of quartz particles ranging from 4 to 30 μ, the proportion of fine material being larger than before. There was no evidence whatever of the presence of amorphous silica, which could easily have been recognized by its low index of refraction, nor was there any evidence of an amorphous film on any of the grains, a condition also easily recognized.[24]

I am inclined to believe that some unrecognized factor has affected the results obtained by Ray, and that mechanical grinding is without measurable effect on the density of quartz.

Dale[25] made experiments similar to those of Ray, using a vein quartz, and obtained the following average results.

[22] Ray, R. C., *The effect of long grinding on quartz (silver sand)*, Proc. Roy. Soc. London (1923) A **102**: 640-642.

[23] Correspondence with the author.

[24] Sosman, R. B., & Merwin, H. E., *The effect of fine grinding on the density of quartz*, J. Wash. Acad. Sci. (1924) **14**: 117-118.

[25] Dale, A. J., *The effect of prolonged grinding on the density of quartz*, Trans. English Ceram. Soc. (1924) **23**: 211-216.

Treatment	Mean diameter mm	d at 22.8°
A. Crushed, sieved between 20 and 60 mesh..	0.46	2.6405
B. Crushed, sieved between 60 and 100 mesh.	0.17	2.6455
Fraction A, ground 6 hours.....	{53% 0.04 {45% 0.006	2.6350
Fraction B, ground 6 hours.....	{51% 0.04 {49% 0.006	2.6290

The quartz was not very pure, analyzing 99.52 per cent SiO_2, with 0.65 per cent as the summation of 8 separately determined impurities. The original densities of the coarse fractions A and B are different, and are 0.1 and 0.3 per cent below that of the purest quartz, indicating possibly the presence of gas bubbles. No microscopic examination of the quartz is recorded. Losses of weight in the agate mortar equivalent to decreases in density of the powders amounting to 0.07 and 0.2 per cent were found. In view of these facts, the observed decreases of 0.2 and 0.6 per cent can not be taken as proof that any of the quartz has been lowered in density or rendered amorphous by the grinding.

Effect of Heating

H. Rose[26] in 1859 tested the effect of high temperatures (and incidentally of the high-low inversion of quartz, although its existence was unknown to him) upon its density. He heated a large clear crystal for 18 hours to the maximum temperature of a porcelain kiln, perhaps 1450°, letting it cool slowly. Aside from a slight opacity on some of the faces, and a few cracks, the crystal was unchanged and its weight remained the same. The original density of the crystal was 2.651, while the final density was 2.650, that is, practically identical with the original. He also observed that the quartz of Flins near Schreibershau, Silesia, which was used for glass-making and was customarily calcined and thrown into water to break it up for that purpose, retained a density of 2.646, practically its original density.

Experimental data on the density of tridymite

It is doubtful whether the density of low-tridymite can be obtained with high accuracy, since each crystal is finely twinned as a result of the high-low inversions, and minute interspaces may exist which are not accessible to the immersion liquid. Their effect, however, should not exceed a small fraction of one per cent.

The best measurements are those by Fenner,[27] by Washburn & Navias,[28] and by Clews & Thompson.[29] The results in true densities are:

[26] Article cited in IV, note [12].
[27] p. 352 of article cited in IV, note [2].
[28] Article cited in X, note [24].
[29] Article cited in V, note [7].

Author	Temp. °C	d	Source
Fenner	27	2.262	
Washburn & Navias	25	2.264	Purified flint and Na_2WO_4 at 1300°
Clews & Thompson	14.1	2.285	Quartz in NaCl melt
	15.5	2.284	

Clews & Thompson's tridymite contained 99.28 per cent SiO_2, 0.26 Al_2O_3, 0.14 K_2O, and 0.08 Na_2O. Their temperature of measurement is about 10° lower than the other two, but the differences in density are too large to be accounted for by thermal dilatation. The discrepancies remain unexplained.

Density of cristobalite

The true density of low-cristobalite is difficult to determine because the product is usually very fine-grained. In any method involving displacement of a liquid, such as the pyknometer or the flotation methods, the aggregates of grains must be broken up, and adhering gases must be removed by evacuating and heating.

Even when this is done carefully and conscientiously, it still remains possible, in a material of this character, that there are interspaces of such small dimensions between parallel-lying grains that the pyknometer liquid will not penetrate into them, and a low apparent density will be the result.

On the basis of the above considerations we should expect that the more carefully the density of a given specimen of cristobalite is determined, or the better crystallized the material on which the determination is made, the more nearly will it approach a certain maximum, which is the true density of cristobalite.

These expectations are realized in most cases, but not always. There remain certain carefully made measurements on well-defined material yielding densities which are clearly lower than equally careful measurements on other material. It seems necessary to conclude that the true crystalline density can vary, just as the inversion-point and other properties are known to vary (see p. 126) with the origin or the temperature of formation of the cristobalite.

The maximum approached by the denser specimens is 2.325.

The uncertainty of the density is greatest in cristobalite produced from a micro-crystalline or finely fibrous variety of silica by the action of high temperatures. The density of such cristobalite may be as low as 2.17, even after fine grinding has opened the pores and evacuation has removed the adhering gases. This value is less even than the density of vitreous silica.

Cristobalite from other sources may have intermediate densities between 2.17 and 2.325, which is the density of well-crystallized material formed with the aid of a flux.

The experimental data on cristobalite of normal or nearly normal density

The best crystals of cristobalite are obtained by the transformation of other forms of silica with the aid of a flux. Determinations on material of this kind, and also on some other cristobalite specimens of nearly normal density, are included in Table XVIII.7.

The cristobalite formed both from vitreous and from amorphous silica by heating in a porcelain kiln (18 hours over 1200°; maximum 1450°) is of nearly normal density and the density is changed very little by continued heating. See Table XVIII.8.

The best measurements are by Fenner,[30] by Day & Shepherd,[31] and by Washburn & Navias.[32]

TABLE XVIII.7.

DATA ON CRISTOBALITE OF NORMAL DENSITY.

Author	Temp. °C	*d*	Mean *d*	Source
Fenner	27	2.325		
Day & Shepherd	25	2.318 2.323 2.318	2.320	Quartz 3 days at 1200°
	25	2.320 2.318	2.319	Quartz 6 days at 1160°
	25	2.309 2.311 2.309 2.312	2.310	Vitreous SiO_2 3 days at 1200°
	25	2.312 2.311 2.309	2.311	Vitreous SiO_2 6 days at 1160°
Washburn & Navias	25	2.324		Purified flint and Na_2WO_4 at 1500°

The experimental data on cristobalite of abnormally low density

The low apparent density of the products obtained by burning flint and hyalite was observed in 1859 by H. Rose, 22 years before cristobalite was recognized and named as a distinct modification. He observed that the "specific gravity" of the flint, originally 2.591, fell to 2.237; while that of the hyalite, originally 2.15-2.16, rose to about 2.20. H. Rose supposed the products to be amorphous, while G. Rose in 1869 considered them to be tridymite, but neither had any good explanation to offer for the low density.

[30] FENNER, p. 354 of article cited in IV, note [2].
[31] DAY & SHEPHERD, p. 1100 of article cited in IV, note [4] (or p. 277 of DAY, SHEPHERD & WRIGHT).
[32] Article cited in XIII, note [24].

An even smaller specific gravity, 2.16, was observed by Le Chatelier in 1890, on agate calcined at 1500°. Endell & Rieke [33] observed 2.16 pyknometrically on cristobalite made by burning Brazilian chalcedony. Washburn & Navias found 2.169 on cristobalite made by burning chalcedony from Yellowstone Park.

Flint, an impure variety of chalcedony, seems to yield a denser cristobalite than does chalcedony itself, as indicated by the following results:

Observer	Source of silica	Temp. °C	*d*
Washburn & Navias	Black French flint	25	2.245
Rieke & Endell	Flint, in fragments		2.226–2.251
Mellor & Campbell	French flint	15	2.22

This effect may be due to the fluxing action of impurities.

Washburn & Navias [34] found that the cristobalite made by heating chalcedony (from Yellowstone Park) for 2 hours at 1430 to 1460° had a density at 25° of 2.169, falling 6.7 per cent below the true density of well-crystallized cristobalite. Their first supposition was that this low apparent density was due to extremely fine interspaces among the cristobalite crystals,—interspaces so small that air-free distilled water would not penetrate them even though admitted to the finely ground powder after it had been heated at 400°C and at the same time evacuated with a mercury-vapor pump. It might therefore be supposed that high hydraulic pressure would fill some of these pores and so yield a higher density. But a pressure of 1000 atmospheres for two hours failed to drive any appreciable amount of water into the interspaces, as shown by the fact that this treatment produced an increase in apparent density of only 0.0006 or 0.03 per cent.

The existence of small interspaces not accessible even to water under high pressure does, however, seem proved by a further experiment. By grinding the low-density cristobalite very fine and pouring off the fraction which remained suspended in water after 48 hours' settling, they obtained a sample which contained particles only 2.3 μ in average diameter and which had a density at 25° of 2.224, only 4.3 per cent below the true density, as compared with 6.7 per cent low for the original specimen. But 4.3 per cent is still a fairly large difference, and it seems necessary to conclude that we have here a real difference in density between cristobalite from different sources.

Effect of repeated heating

The effect of repeated heating on the density of cristobalite made from micro-phases of silica is shown in Table XVIII.8 (data of Rieke & Endell [35]). The cristobalite from chalcedony evidently increases a little in density, perhaps as a result of the growth of crystals accompanying sintering (see Chapter IX). The cristobalite from flint increases a little and then decreases again;

[33] Article cited in V, note [18].
[34] Article cited in XIII note [24].
[35] Article cited in V, note [14].

no reason is known for this behavior. The cristobalite from amorphous and from vitreous silica is nearly normal, and changes but little.

TABLE XVIII.8.

EFFECT OF REPEATED HEATINGS IN A PORCELAIN KILN (MAXIMUM 1450°) UPON THE APPARENT SPECIFIC GRAVITY OF CRISTOBALITE (REFERRED TO WATER AT 20°). RIEKE & ENDELL.

Original form of silica	Chalcedony, in fragments	Flint, in fragments	Amorphous precipitated silica (Kahlbaum)	Vitreous silica (Heraeus)
Original density	2.607	2.632	....	2.21
Sp. gravity after 1 heating	2.16	2.231	2.322	2.327
" " " 2 "	2.17	2.241	2.319	2.328
" " " 3 "	2.17	2.248	2.312	2.33
" " " 4 "	2.19	2.239	2.316	
" " " 5 "		2.233	2.317	
" " " 6 "		2.255		
" " " 7 "		2.251		
" " " 8 "		2.231		
" " " 9 "		2.230		

EXPERIMENTAL DATA ON THE DENSITY OF VITREOUS SILICA

Constancy of the density

The existence of differences in density in vitreous silica is shown clearly by the measurements of Stierlin,[36] consisting of precise weighings in air and water with 3 specimens suitable for optical work. The results, recalculated to true density, are:

Specimen	Temp. °C	*d*	*d* at 0°
Cylinder 15 × 25 mm.....	16.8	2.203 99	
		2.204 08	
		2.204 04	2.204 08
Cylinder 13 × 50 mm.....	22.0	2.202 73	2.202 79
Cylinder 13 × 72 mm.....	22.0	2.202 89	2.202 95

The corrections to 0° I have made with a dilatation coefficient of 1.2×10^{-6}. The dilatation is so small that the correction is hardly appreciable. Each of the three has been corrected for the presence of one or more minute bubbles, amounting respectively to 0.003, 0.032, and 0.002 per cent of the total volume. Evidently the difference of 0.055 per cent between the first specimen and the mean of the second and third is real. Its magnitude is about ten times that of the largest difference known certainly to exist in quartz (see p. 289).

[36] Article cited in note [15].

A similar difference is shown in four determinations[37] by Stumpf, made on homogeneous bars of vitreous silica, 1.4 x 6 x 80 mm, almost free from strain as shown by a mica plate. The measurements were at 18°, and gave the results:

2.2030	2.2031	2.2043	2.2042

The widest difference in this series is 0.0013, or 0.06 per cent.

Not only may there be differences in density between different specimens of vitreous silica, but there are indications of a measurable variation within a given specimen. Rieke & Endell[38] found variations of ± 0.0025, or about 0.1 per cent, in the pyknometric density of powdered vitreous silica, as well as differences of ± 0.002 between the powder, as determined by pyknometer, and larger fragments as determined by the flotation (suspending-liquid) method.

The cause of the variations in density is not known. The most important variable to look out for is the composition, for many specimens of quartz are known to contain minute amounts of alkalies. This would not, however, explain why the variations in vitreous silica are larger than in quartz. It may be possible to correlate them with one or more of the following variables: (1) kind of silica from which the glass was made; (2) temperature to which the glass has been heated in manufacture; (3) state of strain of the glass; but no such correlation has yet been attempted experimentally. That these variables do have an influence we know from their effect on the elastic properties (Chapter XXIII; see also p. 101).

Other data of precision

Besides the measurements by Stierlin and Stumpf, already described, we have data of good precision from Chappuis (1903), and Madelung & Fuchs (1921).

Chappuis[39] found the specific gravity at 0° referred to water at 4° of a 13-gram optically clear lens to be 2.2016.

Madelung & Fuchs[40] measured the density at 0° of an 8.7-gram piece by displacement of mercury and obtained the value 2.1957.

The data reviewed above are assembled in Table XVIII.9 in their order of magnitude. It will be seen that Chappuis' value is about 0.11 per cent less than Stierlin's highest value, while that of Madelung & Fuchs is 0.4 per cent below Stierlin's highest. In the latter case perhaps 0.1 per cent might be accounted for by failure of the mercury to fit the surface (see p. 299) but so large a difference as 0.4 per cent does not seem thus explainable.

[37] Correspondence with the author, Jan. 1925. Mean value is given in article referred to in XXIII, note [12].

[38] Article cited in V, note [14].

[39] Chappuis, P., *Über einige Eigenschaften des geschmolzenen Quarzes,* Verh. Naturf. Ges. Basel (1903) 16: 173-183.

[40] Madelung & Fuchs, reference cited in note [27].

It is fairly certain, then, that the density of such vitreous silica as has been examined is much less constant than that of quartz.

At least 20 other determinations have been published, but the record is in no case complete, lacking the temperature of the water to which referred, indication of the method, or other essential statement. Most of them are, further, of low or doubtful precision, and would add nothing to the data given above.

TABLE XVIII.9.

BEST DETERMINATIONS OF THE DENSITY OF SPECIMENS OF VITREOUS SILICA.

Investigator	True density at 0° C	Investigator	True density at 0° C
Stumpf	2.204 2	Stumpf	2.202 9
Stumpf	2.204 1	Stierlin	2.202 8
Stierlin	2.204 1	Chappuis	2.201 6
Stierlin	2.203 0	Madelung & Fuchs	2.195 7
Stumpf	2.203 0		

DENSITIES OF THE MICRO-FORMS

The density of chalcedony is always less than that of quartz. Definite limits cannot be set unless we first define the difference between "chalcedony" and "impure chalcedony." As this is usually not very exactly defined, the limits given in the mineralogical reference books vary somewhat. In general it may be said that the density under atmospheric conditions is always 2 per cent less than that of quartz and may be as much as 5 per cent less before the mineral is considered too impure to be called "pure chalcedony" according to mineralogical standards.

GENERAL RELATIONS BETWEEN THE DENSITIES OF THE FORMS

It is evident from Table XVIII.1 that the passage from vitreous silica (glass) to cristobalite at 25° is accompanied by a contraction in volume of 5.3 per cent. The further change from cristobalite to tridymite, at the same temperature, involves an *expansion* amounting to 2.6 per cent of the volume of the cristobalite. From tridymite to quartz there is a relatively large shrinkage in volume, namely, 14.6 per cent.

Tridymite, cristobalite, and vitreous silica are not far apart in volume, but are comparatively far removed from quartz.

The relationships between the symmetries of quartz and tridymite, and between both of these and isometric symmetry, already commented upon in the chapter on symmetry (p. 204) may also be expressed in terms of specific volume or density. If we assume a tetragonal unit structure as a basis, and convert it first into a trigonal structure with the dimensions of quartz by shortening one axis, and then into an hexagonal structure having the dimensions of tridymite by lengthening the other two axes, it

results geometrically that the ratio of the density of quartz to that of tridymite [41] should be 1.153. The actual ratio is 1.172.

Densities and isotope ratios

It was shown in Chapter II that there is still a possibility, albeit an unlikely one, that silica is not the same substance everywhere upon the Earth, but that the relative proportions of its three isotopes Si^{28}, Si^{29} and Si^{30} are variable from place to place.

If the atomic volume of the isotopes is the same, which is a reasonable and probable assumption, then the density will vary with the isotope proportion. The density of quartz, which has been often carefully determined, may indicate the limits of variation.

If we assume for purposes of comparison that the atomic masses of the isotopes are exactly 28, 29, and 30, respectively, and that the density of $Si^{28}O_2$ at 20° is exactly 2.645000, then a mixture containing 10 molecules of $Si^{29}O_2$ to every 90 molecules of $Si^{28}O_2$ would have a density of 2.649408 and the silicon obtained therefrom would have an atomic weight of 28.10. A mixture having 89 molecules of $Si^{28}O_2$ to every 11 molecules of $Si^{29}O_2$ would have a density of 2.649849 and an atomic weight for the silicon of 28.11.

The known variability of density among different specimens of clear transparent quartz is not less than 0.000100. If due to varying isotope proportions, this would correspond, under the above assumptions, to a variation of 0.0023 in atomic weight or 0.23 per cent in the relative proportion of Si^{29} to Si^{28}. If the variability of density is as much as 0.000500, which is possible though not probable, the difference in atomic weight would be 0.012. These amounts are on or beyond the limits of accuracy in the determination of the atomic weight, a difficult determination in the case of silicon. Hence the question whether the variable density represents a varying proportion of isotopes will not be answerable by further atomic weight measurements.

Variability in the forms other than quartz

Assuming a constant ratio between the silicon isotopes, the general deduction can be made from the theory of Chapter XV that the densities of quartz and tridymite should be constant within very narrow limits, while the densities of cristobalite, vitreous silica, and chalcedony should be measurably variable.

These expectations are in agreement with the facts, except that the density of tridymite has not been shown to be as constant as that of quartz. This may, however, be due to the small number of determinations and the unsatisfactory character of the material upon which some of the measure-

[41] Beckenkamp, J., *Leitfaden d. Kristallographie* (1919, Berlin), p. 75.

ments were made. The variability of the density of cristobalite, vitreous silica, and chalcedony is well known.

The variations in density of cristobalite have not been correlated with its temperature of formation and it is important that this should be done. Other things being equal, the cristobalite which forms at the highest temperature and has the highest high-low inversion point should be the least dense, but it is possible that the difference will be so small that it will be concealed by the very large differences which arise from the variations in structure of the materials from which the cristobalite has been made (see p. 129).

The abnormally low density of the cristobalite made from micro-forms of silica has already been explained theoretically at p. 273, in describing the mechanism of the transformation of chalcedony into cristobalite.

Washburn & Navias offer what is in effect an alternative hypothesis to explain the low density and low index of refraction of the cristobalite produced from chalcedony, in their suggestion that a continuous gradation is possible from perfectly crystalline cristobalite over to amorphous silica. This has already been considered in XVII and shown to be improbable for most substances but yet a possibility worth considering in the case of so sluggish a substance as silica.

I believe, however, that the simpler explanation at p. 273 will serve equally well and is therefore to be preferred for its simplicity.

Part 4. Thermal Energy

Chapter XIX. THE STORAGE OF THERMAL ENERGY

Heat capacity

Thermal energy is the energy of vibratory motion of atoms, parts of atoms, and groups of atoms. The addition of such energy to an object or a system usually raises its temperature, and we may think of the energy as having been stored in the object. If the storage of the infinitesimal energy dQ in one gram of a homogeneous substance raises the temperature of that one gram by the amount dT, then dQ/dT is the *true heat capacity,* or simply "true heat," of the substance. It will be represented by the symbol c. The heat capacity of a solid differs a little according to whether the one gram is kept under constant pressure or is held at constant volume during the heating (symbols c_p or c_v, respectively).

Latent energy

The effect of putting thermal energy into a system is not always to raise its temperature. If the system is a mixture of ice and water, for example, the only visible change after the energy has been added is that there is more water and less ice than before. The energy has become *latent.* It is evident that this so-called "latent heat" is rather a form of chemical than of thermal energy, depending as it does upon fundamental rearrangements in the relative positions of atoms and of molecules, and therefore associated, in a pure substance, with changes of state such as melting, vaporization, and change from one polymorphous form to another.

The measurement of this latent energy in a substance such as silica, however, depends in most cases upon its conversion into thermal energy. Moreover, as will be shown later, there are difficulties in the definition of latent energy as distinguished from heat capacity in the case of the high-low inversions. These considerations make it desirable to consider the latent heats of silica in the same chapter with its heat capacities.

But even where no visible change of state has occurred, some of the energy must be considered as other than thermal. If the substance expands, its "volume energy" is different. If atomic rearrangements take place within the homogeneous substance its "chemical energy" is different. The effects of such rearrangements may become so noticeable, as in the case of low-quartz, as to deserve the name of "distributed latent heat."[1]

[1] A term suggested to me by Dr. W. P. White.

It is impossible, however, to separate out these different continuous effects quantitatively from the sum total of the heat capacity. They serve to emphasize the elasticity of the boundaries between the kinds of energy classified in Table I (p. 21).

Units

Heat capacity has usually been stated in calories. Several different units have been given the name "calory." The 20°-*gram-calory*, which has been used by many investigators in the United States, may be defined as the quantity of heat required to raise the temperature of 1 gram of water (under 1 atmosphere constant pressure) from 19.5 to 20.5°C on the normal hydrogen scale of temperature.

As thus defined and measured, the heat capacity of a substance is more correctly called the "specific heat," for, like specific gravity, it is only a numerical ratio, referred to water as a standard substance. It is convertible into a real physical quantity, having dimensions of its own, by determining the amount of energy required to raise the temperature of 1 gram of water from 19.5 to 20.5°C. The present generally accepted value of this energy is 4.181 absolute joule. The "15-degree calory" = 4.185 joule and the "mean calory" = 4.186 joule.

Unless otherwise noted, "calory" in this book means the 20°-gram-calory, equal to 4.181 joule, although most of the recorded data on silica are not at present accurate enough to make the difference between the calories worth considering.

Quantitative measure of latent heat

Reference has been made to the familiar fact that at a melting or boiling point the addition of heat energy does not cause an increase of temperature. Instead, it results in the formation of a certain amount of a new phase, while the temperature remains constant. The quantity of energy which disappears during the transformation of 1 gram is called the *latent heat* of the transformation, and is exactly reproduced when the transformation is reversed.

The same considerations apply to an inversion similar to the sluggish type in silica, where two different crystalline phases are in equilibrium (Chapters IV and V), such, for instance, as the inversion of quartz to tridymite at 870°.

Whether the definition in the simple form given above is strictly applicable to the high-low type of inversion (Chapter VII) may be questioned, because there does not seem to be any equilibrium of the usual kind between the two modifications (see p. 112). Just how this type of inversion is logically to be treated must remain an open question until we obtain more information regarding the mechanism of the inversion. We know that there is a measurable absorption of heat at or near the high-low inversion temperature on heating quartz or cristobalite, and a corresponding evolution of heat on cooling. We may look upon this heat effect in either of two ways: (1) We may consider that the curve of true heat

capacity has a sharp maximum at the inversion point, but is not interrupted; or (2) we may consider that there is a real break in the curve of true heat capacity, and may define the latent heat of the inversion as the difference in the total heat H (see p. 348) found by extrapolating upward from a lower temperature and downward from a higher temperature to a common "mean inversion temperature."

The second of the two methods just mentioned has the sounder experimental basis and will be followed here. Careful measurements of the true heat capacity for small temperature intervals near the inversion would be useful in throwing further light on the question.

Latent heats of silica

The most probable values for some of the latent heats of transformation of silica are given in Table XIX.1. I call them "most probable" without any great confidence that they may not be changed by 100 per cent or more within the next few years. The experimental data are very conflicting.

Table XIX.1.

Latent Heats of Transformation of Modifications of Silica.

Transformation	Temperature t °C	Heat absorbed at t	
		cal. per gram	kg-cal. per formula-weight (60.1 g)
High-cristobalite → liquid (fusion)	1710	17	1.0
High-quartz → liquid (fusion)	1710 *	50	3.0
Low-quartz → high-quartz	573	2½	0.15
Low - 1100° - cristobalite → high - 1100° - cristobalite †	230	1	0.06
Low - 1600° - cristobalite → high - 1600° - cristobalite †	270	2½	0.15

* This temperature is not the melting-point of quartz; it is selected merely for the sake of the comparison with cristobalite. The difference in heat content between quartz and vitreous silica at any other temperature can be calculated from this (see p. 318).

† Cristobalites made at different temperatures differ in inversion point and in various other ways.

True heat capacities of silica

In general, the amount of energy required to raise the temperature of a substance from 100 to 101° or from 1500 to 1501° is different from that required to raise it from 0 to 1°. In other words, the heat capacity varies with the temperature. For solid substances this is its principal variation.

The most probable values of the heat capacity of quartz, cristobalite, and vitreous silica, over a wide range of temperature, are given in Table XIX.2 and shown graphically in Figure XIX.1.

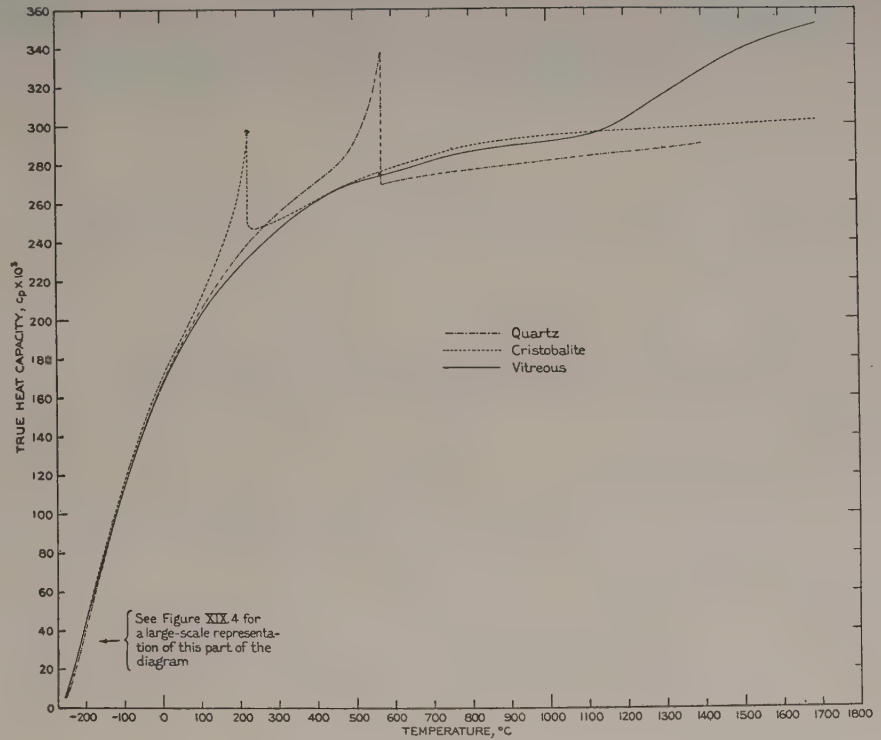

TRUE HEAT CAPACITY, $c_p \times 10^3$
TEMPERATURE, °C
Quartz
Cristobalite
Vitreous
See Figure XIX.4 for a large-scale representation of this part of the diagram

FIG. XIX.1.—Average values for the true heat capacities of quartz, cristobalite (made at 1100°), and vitreous silica.

The cristobalite data apply to material made at 1100°; if made at a higher temperature its heat capacity above its inversion point is higher by a few per cent. The absolute accuracy of the data is not as high as the figures would indicate; further measurements may alter the shape of the curve, and the last place of figures represents only relative precision. There are no data whatever on tridymite.

TABLE XIX.2.

TRUE HEAT CAPACITIES OF SOME OF THE MODIFICATIONS OF SILICA.

Values are $10^3 c_p$ in 20°-gram-calories per gram.

t °C	T °K	Quartz	Cristobalite *	Vitreous silica
—255	18			4.8
—250	23	5.4	6.8	7.7
—243	30	9.4	11.2	12.7
—233	40	16.0	18.2	19.8
—223	50	23.5	25.4	26.7
—200	73	41.0	44.	43.4
—150	123	77.4	81.	79.5
—100	173	111.2	115.	112.8
— 50	223	141.2	145.	142.2
0	273	166.4	170.	165.7
50	323	187.0	189.	185.
100	373	204.3	211.	201.
150	423	219.4	234.	215.
200	473	232.7	262.	227.
250	523	244.4	247.	236.
300	573	254.3	251.	245.
350	623	262.7	256.	254.
400	673	270.0	261.	260.
450	723	278.0	266.	266.
500	773	291.0	271.	270.
550	823	316.0	275.	273.
573	846	340.(?)		
600	873	270.9	278.	275.
700	973	274.0	284.	281.
800	1073	276.7	289.	286.
900	1173	279.3	292.	289.
1000	1273	281.7	293.	292.
1100	1373	283.8	294.	294.
1200	1473	285.5	296.	303.
1300	1573	287.5	299.	316.
1400	1673	290.0	301.	328.
1500	1773		303.	339.
1600	1873		304.	346.
1700	1973		304.	352.

* Made at 1100°.

The slight irregularity in the curve for vitreous silica at about 500 to 700 C may not be real, but due to the form of curve resulting from the averaging of several curves of mean heat which do not agree particularly well (see Fig. XIX.9). Furthermore, it is entirely possible, and even probable, that the true heat capacity of vitreous silica varies with its previous history, just as do its elastic properties, but there have been no

experiments to test this question. On the other hand, there are suggestions here and there of a genuine irregularity in vitreous silica near 600° (see particularly Fig. XXXIV.6).

Mean heat capacity

The true heat capacity has been given first in this chapter because it is the most fundamental thermal constant of a substance and the one of most

Table XIX.3.

Mean Heat Capacities from 0°C of Some of the Modifications of Silica.
Values are $10^3 c_m$ in 20°-gram-calories per gram.

t °C	T °K	Quartz	Cristobalite *	Vitreous silica
—250	23	91.4	95.3	93.6
—200	73	108.7	112.5	110.1
—150	123	125.1	129.	126.
—100	173	140.6	144.	141.
— 50	223	154.3	158.	154.5
0	273	166.4	170.	165.7
50	323	177.0	179.5	176.
100	373	186.4	190.	185.
150	423	194.9	200.	193.
200	473	202.7	212.5	200.
225	498		{219. † {224. ‡	
250	523	209.9	227.	206.
300	573	216.5	231.	212.
350	623	222.5	234.	217.
400	673	228.0	237.	222.
450	723	233.0	240.	227.
500	773	238.0	243.	231.
550	823	243.7	246.	235.
573	846	{247.0 † {251.5 ‡		
600	873	252.3	248.	238.
700	973	255.1	253.	244.
800	1073	257.6	257.	249.
900	1173	259.6	261.	253.
1000	1273	261.7	264.	257.
1100	1373	263.8	267.	260.
1200	1473	265.5	269.	263.
1300	1573	267.2	271.	267.
1400	1673	269.0	273.	270.
1500	1773		275.	275.
1600	1873		277.	279.
1700	1973		279.	283.

* Made at 1100°.
† Low-modification.
‡ High-modification.

theoretical importance. It is not, however, the constant which is usually determined experimentally at temperatures above 0° C. What is usually determined in that range is the total heat given out by one gram of the substance in being cooled from t to t_0; this quantity, divided by the tem-

perature interval $t - t_0$, gives an average constant which is useful in comparing results or making practical calculations. It is called the *mean heat capacity from t_0 to t*, also called the "average heat capacity" or "interval heat capacity" from t_0 to t. t_0 is usually taken as 0°C, and the constant is then called simply the *mean heat capacity from 0°*, or briefly, the "mean heat," represented here by c_m.

If a series of values of H, the total heat content from 0° to t, are plotted against corresponding values of t, an upward-bending curve is usually obtained. The true heat capacity, c, at any temperature t is equal to $\frac{dH}{dt}$, that is, to the slope of the curve itself at t; while the mean heat capacity, c_m, is equal to the slope of the straight line drawn from the origin to the point on the curve at t.

The mean heat is thus more direct a representation of calorimetric data above 0° than the true heat, because it involves no subjective judgment as to the form of the curve of H and t. If the temperatures of measurement are few and far apart, as they usually are, it may be possible to represent the data with equal fairness by several slightly different curves through the points (or by several different empirical equations, which amounts to the same thing). The slope of the curve at a given temperature t may thus become a matter of personal choice and the values selected for the true heat may range more widely from an average value than do those of the mean heat.

This is particularly true of the modifications of silica, which have complex heat-capacity curves because of the occurrence of inversions. It is impossible, for example, to state accurately how the true heat of quartz varies between 500 and 573°C. It increases more rapidly than at lower temperatures, and may reach a very high value near the inversion-point, but the rate of change and the maximum are not well known.

The most probable values of the mean heat of quartz, cristobalite (made at 1100°), and vitreous silica are given in Table XIX.3 and are represented graphically in Figure XIX.2. The remarks in the text concerning Table XIX.2 apply also to Table XIX.3.

Latent heat and heat capacity of micro-crystalline silica

It is not known to what degree chalcedony is a mineral of constant and reproducible properties, hence no such general statements can be made about it as about the principal forms of silica. The difference in heat content between vitreous silica and chalcedony at room temperature is about 35 calories per gram, on the basis of a single set of determinations. This places it much nearer to quartz than to cristobalite.

The true heat capacity of chalcedony is somewhat higher than that of quartz, especially between 0° and 573°, and it evidently has a maximum at or below 573°. The available data are shown in Figure XIX.10, compared with the curve of quartz.

The experimental data

Heat energy is so elusive and unconfinable that its experimental measurement is unusually difficult. No department of physics and chemistry contains more of the type of research which is hopeful and enthusiastic, yet blind to gross errors, than calorimetry. We may therefore be prepared to find, and do find, considerable discrepancies among the thermal data on silica.

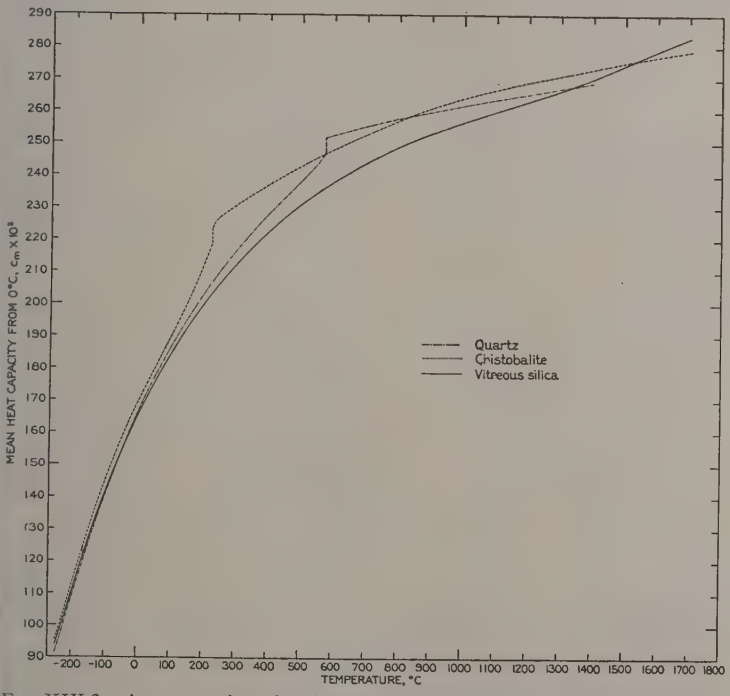


Fig. XIX.2.—Average values for the mean heat capacities from 0°C, of quartz, cristobalite (made at 1100°), and vitreous silica.

Data on latent heats

The values for latent heat of fusion in Table XIX.1 are based primarily on experiments by Wietzel,[2] by Mulert,[3] and by Ray,[4] all of whom

[2] Wietzel, R., *Die Stabilitätsverhältnisse der Glas- und Kristallphase des Siliciumdioxydes,* Zeitschr. anorg. allg. Chem. (1921) **116**: 71-95.

[3] Mulert, O., *Über die Thermochemie der Kieselsäure und der Silikate,* Zeitschr. anorg. Chem. (1912) **75**: 198-240.

[4] Ray, R. C., *Heat of crystallization of quartz,* Proc. Roy. Soc. London (1922) **101**: 509-516.

determined the heats of solution of various modifications of silica in hydrofluoric acid at room temperature. (See Table XIX.4.) This heat of solution varies considerably with the strength of the acid, and may be looked upon as made up of the algebraic sum of a number of different heats of reaction, such as the heats of formation of SiF_4, formation of H_2SiF_6, dissolving of H_2SiF_6, etc.; but if we start with the same initial solution

TABLE XIX.4.

MEASUREMENTS OF THE HEATS OF SOLUTION OF QUARTZ, CRISTOBALITE, AND VITREOUS SILICA.

Substance	Solvent	Heat of solution kg-cal. per 60.3 grams		Difference between glass and crystal	Observer
Quartz (very fine)	Fuming HF	36.48		2.35	Wietzel
Vitreous silica (fine)	" "	38.83			
Quartz (very fine)	35% HF	33.63	33.66	2.31	Wietzel
		33.69			
Vitreous silica (fine)	" "	36.01			
		35.98	35.97		
		35.92			
Quartz (very fine)	20% HF	29.93		2.21	Mulert
Vitreous silica (fine)	" "	32.03	32.14		
		32.25			
Quartz (coarse)	34.6% HF	30.32			
		30.18			
		30.38	30.29		
		30.29			
		30.30		6.95	Ray
Vitreous silica (coarse)	" "	37.33			
		37.04			
		37.27	37.24		
		37.36			
		37.22			
Quartz (fine)	" "	32.47	32.46		
		32.45		4.49	Ray
Vitreous silica (fine)	" "	36.93	36.95		
		36.96			
1600°-cristobalite	35% HF	35.37		0.60	Wietzel
1100°-cristobalite	" "	35.43		0.54	"
Chalcedony (from Iceland)	Fuming HF	36.73	36.72	2.11	"
		36.70			

of HF, and end with the same final mixed solution of H_2SiF_6 and HF, then the subtraction of the total heat of solution of one modification from the total heat of solution of the other cancels out all these partial heats, leaving only the difference in heat content between the two modifications, at room temperature.

Knowing the mean heat capacities of crystalline and vitreous forms between room temperature and the melting-point, we can then calculate the difference in heat content at the melting-point itself (the latent heat). This calculation is exact, depending only on the law of the conservation of energy if the heat capacities are known.

Tammann has shown by measurements of electrical conductivity [5] that the same solution is produced by the dissolving of quartz in HF as by the dissolving of amorphous silica in the same solvent. There is no reason, therefore, to doubt that the heats of solution of the different modifications in HF furnish a reliable basis for the true differences in their heat content.

Quartz

The data for quartz show wide discrepancies, as will be seen in Table XIX.4. The determinations by Wietzel and by Mulert agree fairly well, but Ray found a much larger value, 6.95 kilogram-calories as against their 2.21 to 2.35. I believe that the measurements by Wietzel and Mulert are experimentally the more precise, for they used large volumes of calorimetric liquid of known heat capacity and measured accurately a small rise of temperature (0.5 to 1.5°); while Ray used a small volume of acid (about 25 cc) finishing with a variable end-composition, and measured a large rise of temperature (6 to 34°). The work of Mulert and of Wietzel is certainly better calorimetry than that of Ray, for Ray must have had large errors due to evaporation and convection, as well as uncertainty of composition.

Yet on the face of it the work of Ray should give us the more dependable data for the heat of crystallization of quartz, for the reason that there is an uncertainty in the latent heat data of Mulert and of Wietzel due to the extremely fine subdivision of their materials. Ray used coarse quartz (sand), allowing only part of it to dissolve, and determining the amount dissolved. Mulert and Wietzel attempted to get it all into solution, and in order to accomplish this had to grind and "slime" their quartz and cristobalite. This special treatment should have an effect on the heat of solution (see p. 323).

Nevertheless, I should incline to accept the values by Mulert and by Wietzel as the most probable. Without going into detail at this moment, it will suffice to say that the surprisingly large differences observed by Ray, and ascribed by him to fine grinding, in themselves throw some doubt on his high result.

Mulert's and Wietzel's heats of solution have received some confirmation in experiments by Neumann,[6] who obtained 33.95 ± 0.10 kg-cal. per formula-weight as the average of 3 determinations of the heat of solution of quartz in a 40 per cent solution of HF at 15°C. This may be compared with the values in the third column of Table XIX.4. He has no data on the vitreous under corresponding conditions, so no latent heat can be deduced.

Chernobaev [7] attempted to determine the heat of fusion of quartz by comparing the two different heats of formation of Na_2SiO_3 glass from silica and sodium carbonate, obtained by using first quartz sand and then vitreous silica as the source of the SiO_2. The reaction was:

$$10\,SiO_2 + Na_2CO_3 = (Na_2O.10\,SiO_2)\ (\text{glass}) + CO_2$$

[5] Mulert, O., p. 204 of article cited.

[6] Neumann, Fritz, Neues Jahrb. Mineral. (1925) Beil.-Bd. A **53**: 1-58; Zeitschr. anorg. allg. Chem. (1925) **145**: 193-238, p. 207.

[7] Chernobaev, D., *La chaleur de formation de quelques silicates,* Rev. Metall. (1905) **107**: 729-736.

He employed Le Chatelier's method, which consists in burning a known weight of carbon in contact with the mixture to be studied, in a combustion bomb calorimeter. The high temperature attained by the burning carbon causes the reaction to occur, absorbing or evolving heat which is measured by the calorimeter as a subtraction from or addition to the known heat of combustion of the carbon.

The kilogram-calories absorbed per formula-weight of SiO_2 with the above reaction were:

	Quartz	Vitreous silica	Difference
	9.09	8.93	
	10.23	8.00	
	9.42	9.07	
Mean.....	9.58	8.67	0.91

Inspection of the individual figures will show that the average result is not very reliable, and does little more than indicate the absorption of 1 to 3 kg-cal. per formula-weight of SiO_2.

Chernobaev's attempted determination was thus not very successful, because the quantity sought was a small difference between two large values, both of which were subject to considerable error.[8] But another value for the latent heat which appears at first sight more reliable is obtainable from some of Chernobaev's other data which he himself did not use for the purpose. As Travers[9] points out, one of the reactions mentioned above may be taken together with another reaction measured by Chernobaev to give two independent equations containing the approximate heat of fusion of quartz as an unknown quantity:

$$SiO_2\ (\text{sand}) + Na_2CO_3\ (\text{solid}) = Na_2SiO_3\ (\text{glass}) + CO_2 - 30.4\ \text{kg-cal.}$$

$$10\ SiO_2\ (\text{sand}) + Na_2CO_3\ (\text{solid}) = (9SiO_2.Na_2SiO_3)\ (\text{glass}) + CO_2 - 95.8\ \text{kg-cal.}$$

The subtraction of one of these from the other gives approximately the heat of fusion of the excess 9 formula-weights of SiO_2, whence the heat of fusion per formula-weight is 7.3 kg-cal.

Travers overlooks or disregards the existence of a more siliceous sodium silicate, $Na_2O.2SiO_2$. The "formula" of the glass in the reaction quoted above should perhaps be written $Na_2Si_2O_5.8SiO_2$ instead of $Na_2SiO_3.9SiO_2$, having the latent heat of formation of the disilicate glass from the monosilicate glass as an unknown positive or negative correction. The heat of mixing of liquid SiO_2 and liquid Na_2SiO_3 enters as a further correction. Until these heats are known the above result can not be considered as anything more than a confirmation of the order of magnitude of the quantity.

The figure 135.3 calories per gram is sometimes found quoted as the heat of fusion of quartz. This figure, which is due to Cunningham,[10] is not based

[8] The suggestion is also made by Travers that the glass may have been partly devitrified.

[9] Travers, M. W., J. Soc. Glass Technology (1920) **4**: p. 220.

[10] Cunningham, J. A., Proc. Roy. Dublin Soc. (1901) **9**: 383-414.

on experimental measurement at all but is an estimate of the minimum possible latent heat, derived from two rather qualitative statements by Fremy, namely: (1) The solution of amorphous silica in fuming hydrofluoric acid causes the liquid to boil, and (2) the solution of quartz in the acid gives no measurable heat effect. The second of these statements is so widely in error that Cunningham's estimate is valueless.

Cristobalite

For the heat of crystallization of cristobalite we have only the determinations of Wietzel,[11] and the value in Table XIX.1 is based on these.

Washburn [12] has calculated the latent heat of fusion of cristobalite from the lowering of its freezing point caused by the addition of Al_2O_3. This is discussed at p. 358. The calculation yields a value 6 or 7 times as large as that obtained from heats of solution, but is subject to considerable uncertainty. The best we can say for it is that it indicates a heat of fusion for cristobalite which is no higher than that of quartz but which may be considerably lower.

Chalcedony

The difference between the heat of solution of chalcedony and that of vitreous silica was found by Wietzel to be 2.11 kilogram-calories per 60.3 grams (see Table XIX.4) on a pure specimen of the mineral from Iceland, furnished by Belowsky. He found the corresponding difference for quartz to be 2.33, only 10 per cent higher than for chalcedony, while cristobalite, on the other hand, is only 0.57 kilogram-calories different from the vitreous. Thus there is an approximate equality between the finely ground quartz and the chalcedony.

Latent heats of high-low inversions

As already mentioned (p. 311), we are defining the latent heat of a high-low inversion as the difference between the total-heat-from-0°, as extrapolated upward from near-by points to the inversion temperature, and the total-heat-from-0° as extrapolated downward to this same temperature.

Cristobalite

The values given for cristobalite in Table XIX.1 are from the heat-capacity data of Wietzel.[13] The actual estimates are as follows:

Wietzel (1921)	Cristobalite made at 1100°	1.1 cal.
Wietzel (1921)	Cristobalite made at 1600°	2.8 cal.
White (1919)	Cristobalite made from vitreous above 1500°	2.6 cal.
Cohn (1924)	Cristobalite made from flint	6.0 cal.

The first three estimates are my own; the last is quoted.

[11] Article cited.
[12] Washburn, E. W., J. Amer. Ceram. Soc. (1919) **2**: 1007-1008.
[13] Article cited.

Rieke & Endell [14] observed the heat-evolution of cristobalite, on cooling, at about 228°, with an iron-constantan thermel. Washburn & Navias [15] likewise observed it on cristobalite made from chalcedony and flint, at 220 to 244°. In both these cases, although the amount of heat in calories could not be estimated, it was evidently relatively small, in qualitative agreement with the data given.

Tridymite

There are no quantitative data on the heats of inversion of the tridymites. These heats are probably less than one-fifth as great as the heat of inversion of cristobalite, to judge from Fenner's differential heating curves. The heat-effects on cooling seem to be spread over a range of temperatures for they give hardly detectable effects on a cooling-curve with a differential thermel. It is not surprising, therefore, that Rieke & Endell [16] found on cooling-curves no effect whatever with an iron-constantan thermel reading temperature directly, or that Washburn & Navias detected no heat effect between 105 and 138° with a mercury thermometer.

Quartz

The value assigned to quartz is derived from the heat-capacity tables and curves of the first part of this chapter. An independent check is found in the experiments of Perrier & Roux, which set a maximum of 3.0 cal. per gram (see p. 336). Other estimates are:

White [17] (preliminary estimate, 1909)	4.3 ± 1.0
White (my estimate from data of 1919)	1.7 ± 0.3
Cohn (1924) Norwegian quartz	4.2
Rose quartz	4.1
Hohenbocka sand	4.1

Influence of degree of subdivision on latent heats

Mechanical subdivision

We have seen in preceding chapters that the properties of a substance when it is very finely subdivided, into fragments containing only a few thousand or a few hundred atoms each, may be observably different from its properties when it is in the form of fragments or crystals each containing hundreds of thousands or millions of atoms. This effect may have something to do with the wide differences between different determinations of the latent heats and heat capacities of silica, referred to in the preceding pages of this chapter, although the evidence is by no means complete or satisfactory. It is possible that all the effect is due to fineness, though this is difficult to believe.

[14] Article cited in V, note [14].
[15] p. 579 of article cited in XIII, note [24].
[16] Article just cited.
[17] Wright & Larsen, p. 435 of article cited in VII, note [6].

As already noted, an important point of uncertainty in the latent heat data of Mulert and of Wietzel on the latent heat of quartz arises from the fine state of subdivision of their materials, with accompanying doubts as to whether it had undergone any transformations during its preparation. In order to get all the silica into solution within the short time interval necessary in a calorimetric measurement, both Mulert and Wietzel had to "slime" their quartz, by grinding it very fine and stirring it up with water, allowing the heavier particles to settle and using only that material which remained in suspension. Mulert, employing relatively dilute HF, could use only quartz which had remained in suspension 15 hours.

It was found that vitreous silica could be made sufficiently fine by dry grinding alone, and chalcedony dissolved readily without especially fine grinding.

Quartz

The heat of solution of very fine-grained quartz is fairly certain to differ from that of coarse material. As has been remarked before, the great increase of surface means that a certain amount of work has been done against interatomic cohesion, diminishing the difference in heat content between crystal and liquid (glass). If the effect could be assumed to be about the same for all the modifications, it would disappear from the differences which represent the true latent heats, but this cannot have been exactly true in the experiments quoted since the quartz was undoubtedly much finer than the vitreous silica. The true difference in heat content between vitreous and quartz may therefore be expected to be somewhat larger than the values found by Mulert and by Wietzel.

The preceding paragraph had already been written, when a paper by Ray [18] appeared, reporting a difference in heat content between *coarse* quartz and vitreous silica about three times as large as that found by Mulert and Wietzel. The explanation offered by Ray was that the latter values were low because of fine subdivision.

To investigate this point Ray ground his quartz sand and vitreous silica for 15 hours in an agate mortar. The powders were then fine enough to pass a 200-mesh-per-inch sieve, and dissolved completely in 35 per cent HF solution.

The difference in heat of solution between quartz and glass then came out to 4.49, about two-thirds as large as before, bringing the value down nearer those of Mulert and Wietzel (see the data in Table XIX.4). It appears from these experiments, then, that the fine grinding has something directly to do with the discrepancies in heat of solution, but the simple explanation that the effect is due merely to fine subdivision may not be the whole story.

An important question which naturally suggests itself, but about which there is no record in the published papers of Mulert, Wietzel, or Ray, concerns the conditions under which the quartz was ground. Was it ground dry or under water? If under water, then it seems possible, though improbable, that part of the silica might become hydrated and assume an amorphous or gelatinous form. It would then retain the amorphous form when dried at 500°, as was done by Wietzel,[19] unless perhaps some of it changed to cristobalite

[18] RAY, R. C., article cited in note [4].
[19] WIETZEL, correspondence with the author.

which is not very different from the amorphous in its heat of solution. Such a change from quartz to amorphous silica or cristobalite would account for the different heats of solution found by Wietzel and by Mulert on the one hand, and by Ray on the other.

However, Ray's quartz was ground in the dry state,[20] so that the hydration hypothesis will not apply, unless we can assume that the powder absorbed enough moisture from the air to cause part of it to become hydrated, which seems unlikely. Wietzel's quartz and cristobalite were ground under water,[21] and the hydration hypothesis might apply to the difference between his value and the lower of Ray's values (powdered quartz).

What is needed is more direct evidence, such as is obtainable by microscopic examination, of the effect of grinding quartz, both dry and wet, for a considerable time. The evidence of Johnston & Adams, of Smyth, and of my own experiments in the Geophysical Laboratory, already referred to in the chapter on density (p. 300) is all against the supposition that there is a change in form from quartz to amorphous due to grinding.

Vitreous silica

Wietzel ground his vitreous silica both dry and wet,[22] and observed no difference in the heat of solution. This was to have been expected, since even if the water-ground vitreous silica had been partly hydrated the subsequent thorough drying which preceded the dissolving of the silica in HF would have rendered both samples practically alike.

Thermal subdivision

There is also to be considered another method of subdividing quartz in addition to the purely mechanical method of grinding in a mortar. If a piece of quartz be repeatedly heated above 573° and then quenched, it will pass through the inversion-point while having within itself steep temperature

Table XIX.5.

Heats of Solution of Ignited (Geglüht) and Un-ignited Quartz in HF, in Kg-Cal. per 60.3 Grams.

	In 35% acid	In fuming acid	Mean
Heat of solution of ignited quartz.....	33.8	36.65	
Heat of solution of vitreous silica.....	35.97	38.83	
Diff., vitreous — quartz	2.17	2.18	2.18
Heat of solution of fine-ground quartz, not ignited*	33.66	36.48	
Diff., vitreous — quartz	2.31	2.35	2.33
Effect of ignition.....			0.15

* From Table XIX.4.

[20] Ray, correspondence with the author.
[21] Wietzel, correspondence with the author.
[22] Wietzel, correspondence with the author.

gradients. The resulting stresses break it into small fragments. Intimate twinning is another possible result of the quenching (see Chap. IX).

Recognizing the possible effect of fine subdivision and of twinning upon latent heats and heat capacities, Wietzel tried on quartz this thermal method of pulverizing, the material being afterwards ground and slimed as before. He obtained the data shown in Table XIX.5.

The quartz pulverized by heating and quenching appears from Table XIX.5 to be 0.15 kilogram-calory, or about 6 per cent, nearer in heat content to the vitreous than was the original quartz. It would appear, then, that there has been superposed on the very fine purely mechanical subdivision a still further effect, explained by Wietzel as being due to twinning caused by ignition and quenching. This explanation may be correct, but it is by no means proved by the data. I believe an equally probable explanation is that some of the quartz was converted into cristobalite during the ignition, and since cristobalite differs much less from vitreous than does quartz, this partial conversion would explain the apparent approach of the "twinned" quartz toward the vitreous. About 8 per cent of cristobalite would produce the effect observed.

Supposed effect of fine subdivision upon the high-low inversion

According to Wietzel, the automatic pulverizing and twinning of quartz by heating and quenching not only has the effect (1) of decreasing the difference in heat content between vitreous silica and quartz (heat of fusion), but it also (2) decreases the heat of inversion, and (3) causes a rounding off of the sharp maximum of heat capacity at 573°.

Concerning the interpretation of the mean heat data in Table XIX.5, Wietzel[23] states that "no heat of inversion could any longer be determined." But when the experimental determinations in question are plotted with the rest of the data, as in Figure XIX.10, it is evident that they can be interpreted as belonging to high-quartz which has inverted below about 565° instead of at 573°, and which has a somewhat smaller heat content than Wietzel's other two coarse-crystalline specimens, differing from them about as much as they differ from each other. The inference that there was no heat of inversion whatever is not justified.

The experimental data on heat capacity

In discussing the experimental data on the heat capacity of silica it is important to distinguish two very different methods for its determination. One is the *direct-heating* method, the other the *transfer* method, usually called the "method of mixtures."

In the direct-heating method a measured amount of heat energy is put into the substance, and its rise of temperature is then measured. If the temperature interval is small, this method gives the *true heat capacity* directly.

In the transfer method the body is heated to a known temperature and then transferred to a calorimeter, in which the heat content of the body is

[23] Wietzel, R., p. 83 of article cited.

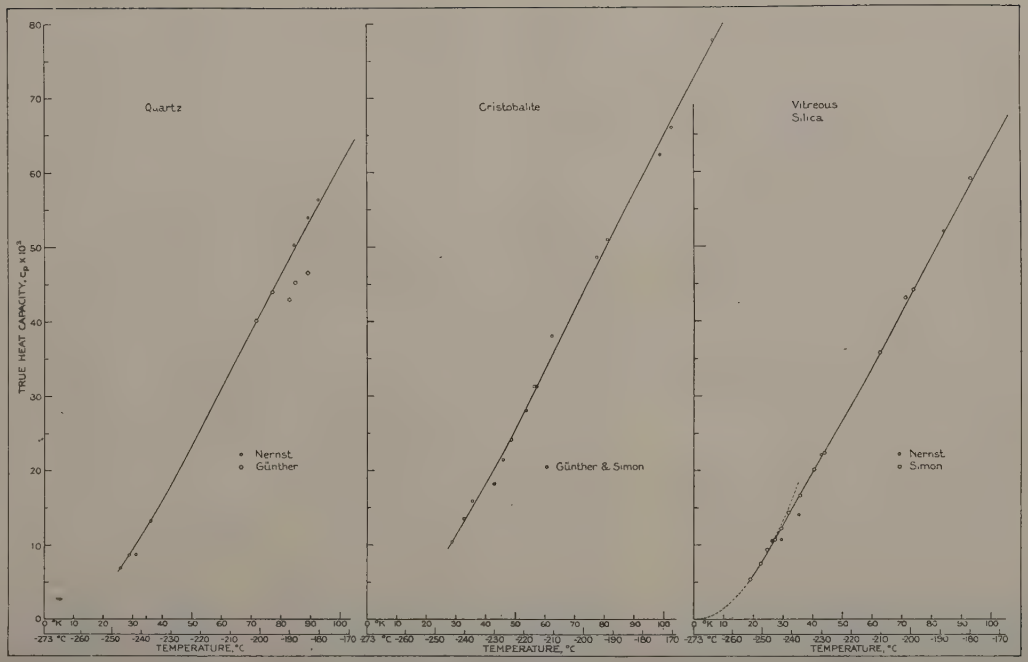


FIG. XIX.3.—Experimental data on the true heat capacities of quartz, cristobalite (made at 1100°) and vitreous silica, from —255 to —150°C.

then measured by the change of temperature of the calorimeter substance (usually water) to which the body has given up its heat. This method gives directly the *mean heat capacity from atmospheric temperature.*

The direct-heating method yields the true heat as the result having primary accuracy, from which the mean heat may be obtained by calculation, but with secondary accuracy. The transfer method, on the contrary, yields the mean heat as the result having primary accuracy, from which the true heat may be obtained by calculation, but with secondary accuracy.

The direct-heating method is most used below 0°C; the transfer method, above 0°C. We have the practical problem, then, of matching the two sets of curves at 0°.

Data below 0°C

The only measurements of true heat capacity below 0°C are those of Nernst,[24] of Simon,[25] and of Günther.[26] The ranges of temperature covered are as follows:

Quartz: Nernst 26 to 93°K, Günther 72 to 89°K.
Cristobalite: Günther and Simon 29 to 198°K.
Vitreous: Nernst 26 to 84°K, Simon 19 to 288°K.

All these measurements were made by observing the rise of temperature produced by the introduction into the specimen of a known amount of heat energy, usually introduced electrically.

For convenience of comparison the low-temperature data are plotted in Figures XIX.3 and XIX.4. Figure XIX.3 separates the measurements for the three substances. Figure XIX.4 combines the three curves into one diagram in order to show their interrelation, and shows also a few measurements of true heat which were beyond the range of Figure XIX.3.

The balancing of systematic and of accidental errors at temperatures below 0°C is such that the region of most exact measurement lies in the range 40 to 120°K (—230 to —150°C). The accuracy in this range is estimated at ½ to 1 per cent, while below and above this it is 1 to 1½ per cent.

The low-temperature data on silica are not entirely satisfactory, although they are a welcome and valuable addition to our knowledge in a field in which experimentation is difficult and high precision not yet to be expected. There is a large unexplained discrepancy in Günther's data on quartz, and there are irregularities in the data on cristobalite and vitreous silica which leave it somewhat uncertain just which of the two has the higher heat capacity at the low temperatures, although on the whole the heat of the vitreous seems a little the higher.

Between —150 and 0°C data are scarce, and the course of the curves is somewhat in doubt. The complete curves of true heat from the lowest temperatures to about 50°C, shown in Figure XIX.4, are a compromise between

[24] Nernst, W., *Der Energieinhalt fester Stoffe,* Ann. Physik (1911) (4) 36: 395-439, p. 421.

[25] Simon, F., *Untersuchungen über die spezifische Wärme bei Tiefen Temperaturen,* Ann. Physik (1922) (4) 68: 241-280.

[26] Wietzel, R., p. 88 of article cited in note [3].

the most probable course of the curves of true heat as extrapolated from above or below, and a few low-temperature measurements of the mean heat from

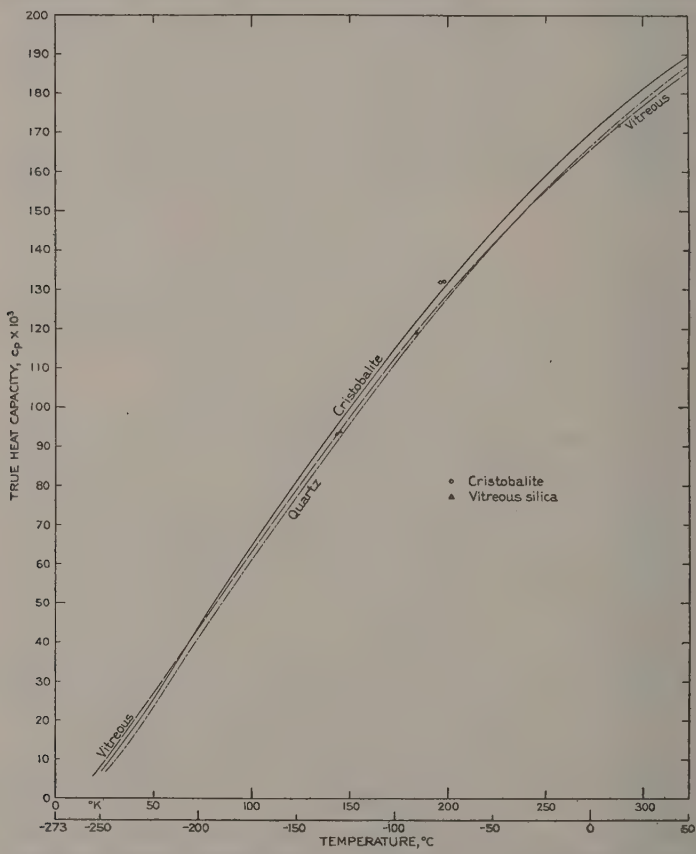


FIG. XIX.4.—Most probable course of the curves of true heat capacity between —255 and 50°C, for the modifications of silica. A few experimental data are indicated which were beyond the range of Figure XIX.3.

0°C. The latter consist of measurements of the mean heat for quartz and vitreous silica by Koref [27] covering two intervals, approximately —193° to —79°C, and —77° to 0°C. There is also one determination by Stierlin [28] of

[27] KOREF, F., *Messungen der spezifischen Wärme bei tiefen Temperaturen mit dem Kupferkalorimeter*, Ann. Physik (1911) (4) **36**: 49-73.
[28] STIERLIN, H., article cited in XVIII, note [15].

the mean heat of vitreous silica for the interval —77° to 18°C. I have recalculated these data to mean heats from 0°C; the results are contained in Table XIX.6.

TABLE XIX.6.

MEAN HEAT CAPACITIES FROM 0°C AT TEMPERATURES BELOW 0°.

	Quartz		Vitreous	
	t	$10^3 c_m$	t	$10^3 c_m$
Koref (1911)	— 76.3	146.1	— 77.4	147.1
	—193.0	111.5	—193.0	112.1
Stierlin (1907)			— 76.9	148.5

In order to compare conveniently these latter data with those on true heat it is necessary to integrate the true-heat-capacity curves from 0°. Unfortunately the measurements for quartz and cristobalite have not been carried up to 0°; but those for the glass have been, and downward extrapolation of the mean heat data above 0° indicates that the true heat of quartz at 0° is a little higher than that of the glass, while cristobalite is higher still.

I have therefore made the comparison in the following way. Tentative true-heat-capacity curves for all three were drawn from the lowest temperatures up to 0°, and were integrated with a Coradi integrator. The mean heat from 0° could then be calculated and plotted, and the data of Koref and of Stierlin could be compared with the curves. The curves of true heat as first drawn were then altered slightly to get better agreement with the data of Koref and of Stierlin, and the integration repeated. A third approximation sufficed to bring the two sets as near agreement as seems possible.

The Koref data agree very well with the curve at —193°C, but seem to be a little low at —78°C, while Stierlin's figure is high. The comparison is shown in Figures XIX.5 and XIX.9. On the whole, the agreement is good.

OLDER DATA ABOVE 0°C

The earliest determinations of the heat capacity of silica for the temperature interval 0 to 100°C are those of Neumann[29] on quartz, in 1831, but the measurements are too low in precision to be worth considering here. The same is true of measurements of the mean heat from 20° to 50° by Kopp (1865) on quartz and hydrated silica; on quartz from room temperature to 100°, by Herschel & Lebour (1878); also by C. Lang (1878) and by Ulrich (1894) on quartz sand.

Regnault's determinations[30] at 100° on quartz (1841) seem to be of better precision, and his mean value, corrected to 0°, is included among the data compared in Figure XIX.5.

R. Weber[31] gives the formula $c = 0.1754 + 0.0004\ t$ for the mean heat

[29] NEUMANN, F. E., Ann. Phys. u. Chem. (Pogg.) (1831) **23**: 1-39.
[30] REGNAULT, V., *Recherches sur la chaleur specifique*, etc., Ann. Chim. et Phys. (1841) (3) **1**: p. 148.
[31] WEBER, R., Bull. Soc. Sci. Nat. Neuchatel (1895) **23**: 17-22.

capacity of quartz from 0°. From comparison with other determinations by the same author it seems probable that this formula is based upon only two temperatures, but as no details are available,—not even the temperatures of measurement,—the result is valueless for present purposes.

The results of Bartoli [32] on quartz agree well with those of White at 100°, but at 312, 417, and 530° they are about thirty per cent higher than any others. As details are lacking the reason for these high results is not evident. No weight has been given them in this summary.

Newer data above 0°C

Leaving out of account the older and less accurate data just reviewed, we may proceed to the consideration of the high-temperature data upon which the final estimate of the most probable values for the heat capacity (see Table XIX.3) are based.

To permit of graphic comparison of the experimental data above atmospheric temperatures, the better data have been plotted; for quartz, in Figures XIX.5, XIX.6, and XIX.7; for cristobalite, in Figure XIX.8; for vitreous silica, in Figure XIX.9; and for chalcedony, in Figure XIX.10.

Measurements on two or more of the forms

Simultaneous measurements on two or more forms of silica have been made by Schulz (1912), Magnus (1913), Lashchenko (1913), White (1919), Wietzel (1921), and Cohn (1924).

The most reliable heat data at temperatures above 0°C are those of White,[33] covering quartz, one variety of cristobalite, and vitreous silica. Systematic errors, which require eternal vigilance, were most carefully studied experimentally by White, instead of being simply estimated or calculated, as has been usual in calorimetric work. His absolute accuracy appears to be better than 0.3 per cent at all temperatures. He used the transfer method with a water calorimeter and multiple-junction thermel, heating the substances in a platinum resistance furnace. Measurements were made on quartz at 8 temperatures (100 to 1100°C), on cristobalite at 8 temperatures (100 to 1400°), and on vitreous silica at 5 temperatures (100 to 900°). The results are summarized in Table XIX.7. The data for quartz agree with 11 measurements at 100 to 1100° made in 1909,[34] within the limits of these somewhat less accurate earlier results.

White's data on the mean heat from 0°C, for quartz and vitreous silica at 100°, 300°, and 500°C, fall on the following parabolic curves (see Table XIX.7 for unit):

Quartz: $10^3 c_m = 168.5 + 0.194\ t - 0.000\,11\ t^2$

Vitreous silica: $10^3 c_m = 167.0 + 0.189\ t - 0.000\,125\ t^2$

[32] Bartoli, A., Bull. Mens. Accad. Gioenia Sci. Nat. Catania (1891) No. 17: 4-8.

[33] White, W. P., *Silicate specific heats, second series,* Amer. J. Sci. (1919) (4) 47: 1-43.

[34] White, W. P., Amer. J. Sci. (1909) (4) 28: 334-346.

The data of Wietzel [35] cover more substances than those of White (quartz, two varieties of cristobalite, chalcedony, and vitreous silica) and also cover a wider temperature range. He used the transfer method with a water

TABLE XIX.7.

MEAN HEAT CAPACITY FROM 0°C OF FORMS OF SILICA. WHITE, 1919.

Results are in gram-calories, 1 cal. = 4.184 joule. Figures in parentheses give number of determinations.

t	Quartz $10^3 c_m$	Cristobalite $10^3 c_m$	Vitreous $10^3 c_m$
100	186.8 (15)	188.3 (3)	184.6 (2)
300	216.8 (5)	233.4 (2)	212.4 (2)
500	237.9 (12)	242.6 (2)	230.3 (2)
550	243.9 (2)		
600	251.1 (5)		
700	254.3 (2)	250.9 (2)	242.3 (4)
900	259.6 (7)	256.9 (2)	251.2 (3)
1100	264.1 (2)	262.5 (2)	
1300		266.2 (2)	
1400		268.0 (2)	

TABLE XIX.8.

MEAN HEAT CAPACITIES FROM 0° OF SEVERAL FORMS OF SILICA. WIETZEL, 1921.

Values are $10^3 c_m$ in 20°-gram-calories per °C.

t °C	Quartz	Quartz from Carrara	Cristobalite made at 1600°	Cristobalite made at 1100°	Vitreous	Chalcedony
100	186.2		189.8		185.2	196.7
200	203.3		212.7		200.8	211.7
225				{218.2 * {221.4 †		
250	211.3		{224.3 * {235.7 †	227.0	207.0	217.2
400	229.0		243.0	236.9	223.1	232.7
565	247.2	246.7				
575	{248.2 * {252.9 †	248.0 255.2	250.9		236.8	251.3
600	253.3	255.5	252.4	248.4	238.7	252.6
800	258.8	259.6	260.4	257.3	250.9	259.3
1000	263.4	263.4	266.0	264.4	258.8	263.7
1200	266.8		270.9	268.9	262.8	270.2 ‡
1400	270.0		274.7		270.1	
1600			277.9		279.3	
1700			279.		283.	

* Low-modification.
† High-modification.
‡ Converted to cristobalite.

calorimeter, but dropped the substance into a copper tube surrounded by water instead of into the water itself. The calorimeter temperature was measured with a platinum resistance thermometer. Measurements were made at 14

[35] WIETZEL, R., article cited in note [2].

temperatures, from 100 to 1700°C. The relative precision is given as ¼ per cent from 200 to 600°C, and ½ per cent above 600°, but only the average results have been published.

Wietzel made at high temperatures a correction which is questionable. By dropping his empty platinum crucible from the furnace at 1500° into the calorimeter, he found that it cooled about 100° by radiation. If the

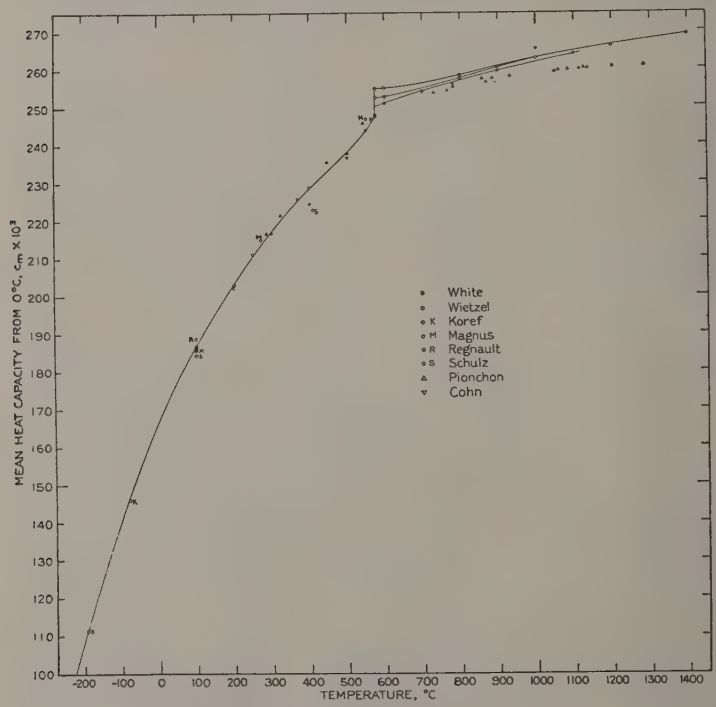


FIG. XIX.5.—Experimental data on the mean heat capacity from 0°C, for quartz. (The curve below 0° is that of Figure XIX.4.)

crucible containing the substance had cooled at the same rate during its fall, no correction would have been needed, as the effect of the lost radiated heat is eliminated by subtraction of the blank determination on the crucible. But the presence of a charge of silica of 15 times the heat capacity of the crucible might, at first sight, seem to have the effect of maintaining the crucible at a higher temperature during its fall and thus increasing its radiation; for this supposed difference Wietzel made a correction of 0.1 per cent at 1100° and 0.65 per cent at 1700°C. Now White shows that the thermal conductivity is such that during its brief time of fall the crucible cools at practically the same

rate whether it is filled with silica or not. Wietzel's correction was therefore unnecessary and made his mean heat at 1700° too high by 0.6 per cent.

Wietzel's average results, with the above-mentioned correction eliminated, are given in Table XIX.8 in 20°-calories.

Schulz [36] measured the mean heat of quartz and vitreous silica from about 20° at three temperatures, approximately 100°, 250°, and 410°C. The heat content was measured by the transfer method in the usual manner, with a water calorimeter.

Magnus [37] likewise measured the mean heat of quartz and vitreous silica from about 17° at three temperatures, approximately 100°, 270°, and 550°C. The substances were contained in a silver vessel which was dropped out of the furnace into a vacuum-insulated copper block.

I have calculated the mean heats from 0° from the published data of both Schulz and Magnus, with the aid of White's formulas (p. 330). The results are given in Table XIX.9 and are plotted in Figure XIX.5.

Table XIX.9.

Mean Heat Capacities from 0° for Quartz and Vitreous Silica, According to Schulz (1912) and Magnus (1913).

	Quartz		Vitreous	
	t, °C	$10^3 c_m$	t, °C	$10^3 c_m$
Schulz	100.04	184.4	100.4	182.7
	99.75	184.1	100.2	182.5
	248.	205.8	249.	202.7
	410.	222.7	413.	217.9
Magnus	99.	185.8 *	99.	184.9 †
	273.5	214.9 *	268.3	209.9 †
	551.	246.9 †	551.	236.5 *

* Mean of 2 measurements.
† Mean of 3 measurements.

The method used by Cohn [38] was quite different in principle from those already described. The heat capacity, as well as the latent heat of inversion, was determined from the rate of change of temperature of a definite quantity of the material when contained in a platinum crucible within an electric resistance furnace under standardized conditions, and subjected to a known temperature gradient between the furnace wall and the crucible. The set-up was calibrated in terms of a substance (a specimen of fired clay) whose heat capacity had been measured in the usual manner by Heyn, Bauer, & Wetzel.[39] The results are therefore dependent upon the accuracy of that measurement. The results further involve the assumption that the thermal conductivity of

[36] Schulz, K., *Ueber die mittlere spezifische Wärme von Quarz und Quarzglas . . .* Centralbl. Mineral. **1912**: 481-491.

[37] Magnus, A., *Messungen spezifischer Wärmen fester Körper bei hohen Temperaturen,* Physik. Zeitschr. (1913) **14**: 5-11.

[38] Cohn, W. M., J. Amer. Ceram. Soc. (1924) **7**: 359-376, 475-488, 548-562; (silica at pp. 482, 485-488).

[39] Mitt. Königl. Materialprüfungsamt (1914) **32**: 89-198.

the standard and the test are sufficiently alike to have no effect upon the rate of temperature-change.

In view of the commonly experienced variability of electric furnaces at high temperatures, the results obtained are much more consistent than I should have expected. I have recalculated the original data into the form of mean heat capacities from 0°, and collected them in Table XIX.10. Because of the indirect character of the method the results can hardly be given as much weight as those of White and of Wietzel, with which in general they agree, although there are some deviations.

TABLE XIX.10.

HEAT CAPACITIES OF FORMS OF SILICA, AS MEASURED BY COHN, 1924.

Values are of $10^3 c_m$.

t °C	Norwegian quartz	Rose quartz	Hohenbocka sand *	Cristobalite	Chalcedony	Micro-amorphous
100	187	187	187	185	166	202
200	203	201	202	205	172	217
300	215	212	212	231	174	230
400	225	223	220	233	177	241
500	237	237	231	240	184	250
600	253	253	248	245	188	257
700	255	254	252	248	192	262
800	258	257	256	253	197	266
900	261	261	260	257	202	270
1000	266	265	265	263	209	275
1100					218	

* 99.95 per cent SiO_2.

Lashchenko [40] measured the mean heat of quartz, chalcedony, and opal at various temperatures up to 900°C. He used the transfer method, with a water calorimeter. The results are not very precise and are so irregular that they are not included in Figure XIX.5. The author himself states that "the primary object was not to determine the absolute specific heat, but to determine the change in specific heat with temperature." The results do show the existence and approximate temperature of the high-low inversions, but cannot be depended upon for an accurate measure of the heat of inversion. From the description of the apparatus and method it seems likely that at least a part of the errors arose from the heating of the substances in a rather wide furnace and from allowing insufficient time for the attainment of constant and uniform temperature.

Since most of the investigators have made measurements at or near 100°, a comparison of the results at that temperature is of interest. This will be found in Table XIX.11.

The data on quartz

The measurements of White, Wietzel, Schulz, and Magnus have just been described. In addition, we have measurements on quartz alone by Joly (1886), Pionchon (1888), and Perrier & Roux (1923).

[40] LASHCHENKO, P. N., Journ. Russian Phys.-Chem. Soc. (1910) **42**: 1604-1614; Bull. Inst. Polytechn. Don (1913) **2**: 8-46.

Joly's measurements [41] were at 100° only, made by the rarely-used condensation method, in which the cold object is placed in steam and its heat capacity from atmospheric temperature to 100° determined by the amount of water condensed in raising its temperature.

Pionchon [42] measured the heat capacity of quartz at intervals of about 50° from 280° to above 1200°C. He used the transfer method with (presumably)

TABLE XIX.11.

COMPARISON OF DETERMINATIONS OF MEAN HEAT CAPACITY FROM 0°, AT 100°C.

Values are $10^3 c_m$ in 20°-calories per gram. Figure in parenthesis gives number of determinations.

		Quartz	Cristo-balite	Vitreous	Chalcedony
Regnault	1841	189.0(3)			
Joly	1886	185.9(4)			
Bartoli	1891	186.			
Dieterici	1905			184.7	
Heinrichs	1906			185.4(8)	
Stierlin	1907			187.2	
White	1909	184.7(2)			
Schulz	1912	184.3(2)		182.6(2)	
Magnus	1913	186.0(2)		185.1(3)	
Wüst and others	1918			199.5(2)	
White	1919	186.9(15)	188.4(3)	184.7(2)	
Bornemann & Hengstenberg	1920			188.3(4)	
Wietzel	1921	186.2	189.8	185.2	196.7
Cohn	1924	187. (3)	185.		166

a water calorimeter. Temperatures were measured by Violle's method, namely, dropping a mass of platinum out of the furnace into another calorimeter and so measuring the heat carried by the platinum. Violle's temperature scale and his heat-capacity curve for platinum are now known to be considerably in error, and I have therefore recalculated Pionchon's data using White's [43] heat curve for platinum as a basis. The results are included in Figure XIX.5. The recalculated results, in the lower half of the range of temperature covered, prove to be fairly consistent with later work.

A single value by Stierlin [44] for quartz at higher temperatures, namely, 0.2448 at 609°C, is abnormally low, coming as it does just above the inversion-point, where the mean heat from 0° rises sharply. The measurement was made on "fine quartz sand prepared from rock crystal." There is no evident reason why the value should be so far off, but without further confirmation it cannot be given any weight.

The measurements of Perrier & Roux [45] are rather different in character

[41] JOLY, J., *On the specific heats of minerals,* Proc. Roy. Soc. London (1886) **41**: 250-274.

[42] PIONCHON, *Sur la variation de la chaleur spécifique du quartz avec la température,* Compt. rend. Acad. Paris (1888) **106**: 1344-1347.

[43] WHITE, W. P., Phys. Rev. (1918) **12**: 436-441.

[44] STIERLIN, H., article cited in XVIII, note [15].

[45] PERRIER, A., & ROUX, H., Mem. Soc. Vaudoise Sci. Nat. (1923) **1**: 109-136. Abstr. in Arch. sci. phys. nat. (1923) (5) **5**: 310-312.

from those just described. Perrier & Roux used the direct-heating method, usually employed only at very low temperatures. By this means they obtained the true heat directly, and were enabled to study its changes in the vicinity of the inversion-point.

In a furnace maintained at a steadily rising temperature they placed the specimen of quartz, inclosed in a jacket of silver, and heated by a winding of silver wire carrying a current. By means of a wattmeter and stop-watch the energy input was measured which was required to increase the temperature of the quartz by 10°. A separate series in blank served to determine the energy required by the jacket, etc. The specimen of quartz was in the form of a plate 53 x 33 x 8 mm, weighing 27 grams. The measurements include 4 series, totaling 69 observations on 10° intervals, and covering the range from 428 to 652°C.

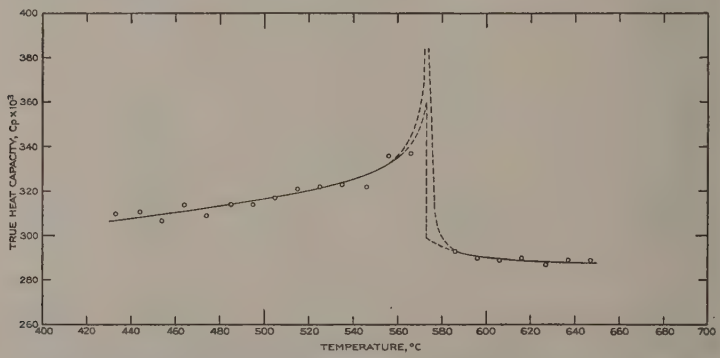


FIG. XIX.6.—Experimental data on the true heat capacity of quartz near its high-low inversion temperature. Perrier & Roux.

In the interval from 570 to 580° the method was not exact because of the differences in temperature which arose from the absorption of heat at the inversion. A special set of 15 measurements was therefore made in the interval 563 to 586°, in which the heating current of the jacket was varied in such a way as to equalize the temperature of jacket and quartz.

These measurements may be interpreted as indicating a very rapid increase in the true heat capacity within two or three degrees of the inversion point, and an equally rapid decrease just after the inversion. They also indicate the existence of a real latent heat of inversion, because the change of true heat capacity is too sharp to account for all of the heat absorbed in the region near the inversion.

The data on the 10° intervals are plotted in Figure XIX.6. , The form of the curves just below and above 573° is a matter of interpretation (see p. 311). We may suppose that the heat capacity rises rapidly to relatively high values (about 1.6 as drawn by Perrier & Roux) but has its high values only over a very short interval of temperature. Or we may suppose that the rise is not so large, and that the heat absorption is a true latent heat.

Perrier & Roux's observations give some definite information about the possible magnitude of this latent heat. The total heat absorbed in an interval of 3° within which the inversion is included was found to be 3.83 calories per gram. Cruder estimates from the series of measurements on 10° intervals gave the purely confirmatory value 4.8. The value 4.0 may be accepted as nearly correct. This places an upper limit on the latent heat, namely 3.0 calories per gram, if we assume 0.33 as the average true heat capacity through the 3° interval. If the average is greater than 0.33, then the latent heat is less than 3.0.

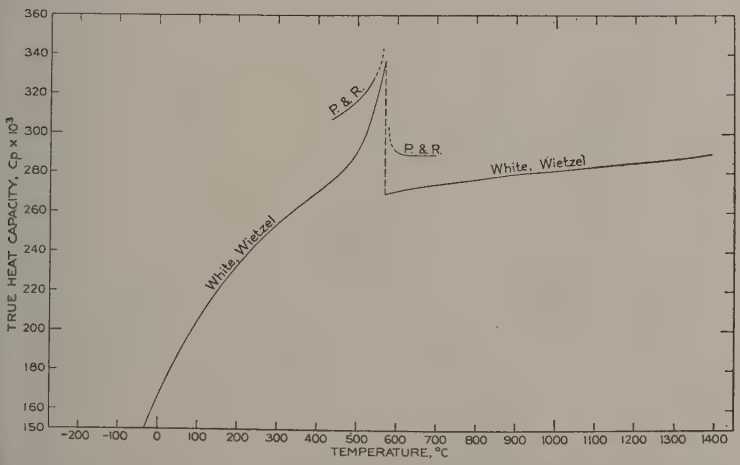


FIG. XIX.7.—Comparison of data of Perrier & Roux (Figure XIX.6) with true heat-capacity curve derived from data on mean heats, represented in Figure XIX.5.

Comparisons

The data of White and of Wietzel are in fairly good agreement, and furnish the principal basis for the general curve adopted above 0°. The two Wietzel curves above 573° represent two different specimens of quartz, the higher being from Carrara, the other of unknown origin. The data of Magnus are a little high, those of Schulz rather low. Pionchon and Cohn are confirmatory.

The data of Perrier & Roux can be brought into the comparison only by deriving the curve of true heat capacity from the White-Wietzel data. This has been done in Figure XIX.7. It is seen that the Perrier-Roux data are high, by more than the apparent experimental error of either set. The curve based on White and Wietzel is probably the more reliable, since they measured total heats from 0° by familiar methods of known accuracy. The ingenious experiments of Perrier & Roux, on the other hand, furnish

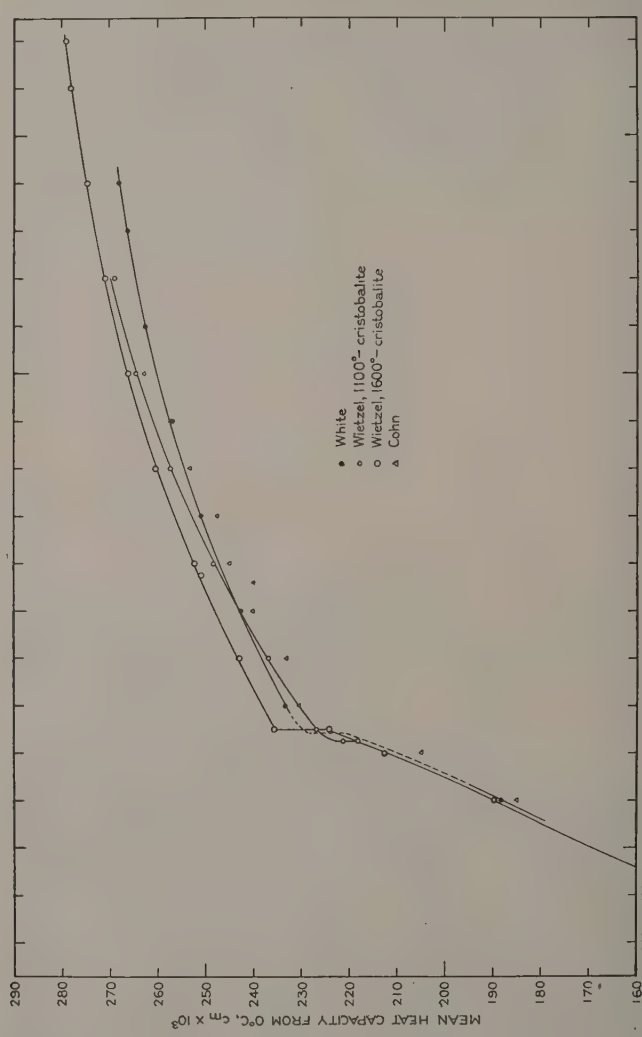


FIG. XIX.8.—Experimental data on the mean heat capacity from 0°C, for cristobalite.

useful information about the inversion-point which can not be so well obtained from the other data.

The data on cristobalite

The measurements of White, of Wietzel, and of Cohn have already been described. The first two sets are plotted in Figure XIX.8. The data of Cohn are much less regular than the foregoing and are evidently less precise; they are included in the Figure, but no attempt is made to represent them by a curve.

The data on vitreous silica

The measurements of White, Wietzel, Schulz, and Magnus have been described (p. 330). In addition, there are available measurements by Dieterici (1905), Heinrichs (1906), Stierlin (1907), Lashchenko (1913), Wüst, Meuthen, & Durrer (1918), Hildebrand & others (1918) and Bornemann & Hengstenberg (1920).

The results of Dieterici [46] on vitreous silica were obtained incidentally to his measurements of the heat capacity of water. The measurements were made at 10 temperatures from 18 to 303°, by the transfer method, with an ice calorimeter. The results are precise to 0.2 per cent. I have recalculated them to 20°-calories for use in Figure XIX.8 by the use of a Bunsen mercury constant of 15.47. The recalculated results are best represented by the empirical formula

$$10^3 c_m = 168.14 + 0.1753\ t - 0.000\,1027\ t^2$$

Heinrichs made 50 determinations at various temperatures from 12 to 320°, with an ice calorimeter, on fragments of a bulb and tube from Heraeus. The results have been recalculated in the same manner as Dieterici's.

The measurements of Heinrichs [47] together with one determination by Dieterici are the only recent data for temperatures in the interval between 0 and 100°C.

Stierlin [48] made some careful measurements of the mean heat capacity of vitreous silica from about 20° at a series of temperatures, including —77°C and every 100° up to 900°C. The transfer method was employed in the usual manner, with a water calorimeter. The mean heats plotted in Figure XIX.8 I have calculated from the author's published values of heat content from 20°C. The systematic correction for radiated heat amounted at the maximum to 1.1 per cent. The accuracy seems to be well within 1 per cent.

Hildebrand [49] made 2 determinations at 320° by the transfer method, obtaining the values 0.2161 and 0.2162, equivalent to 0.2123 from 0°.

[46] Dieterici, C., Ann. Physik (1905) (4) **16**: 593-620.
[47] Heinrichs, J., Inaug.-Diss. Bonn (1906), 59 pp., 2 pls.
[48] Stierlin, H., article cited in XVIII, note [35].
[49] Hildebrand, Duschak, Foster, & Beebe, J. Amer. Chem. Soc. (1917) **39**: p. 295.

Bornemann & Hengstenberg,[50] in connection with a study of the heat capacities of sulfides, determined the heat capacity of vitreous silica in the form of opaque tubing made by the Deutsche Ton- und Steinzeug-Werke of

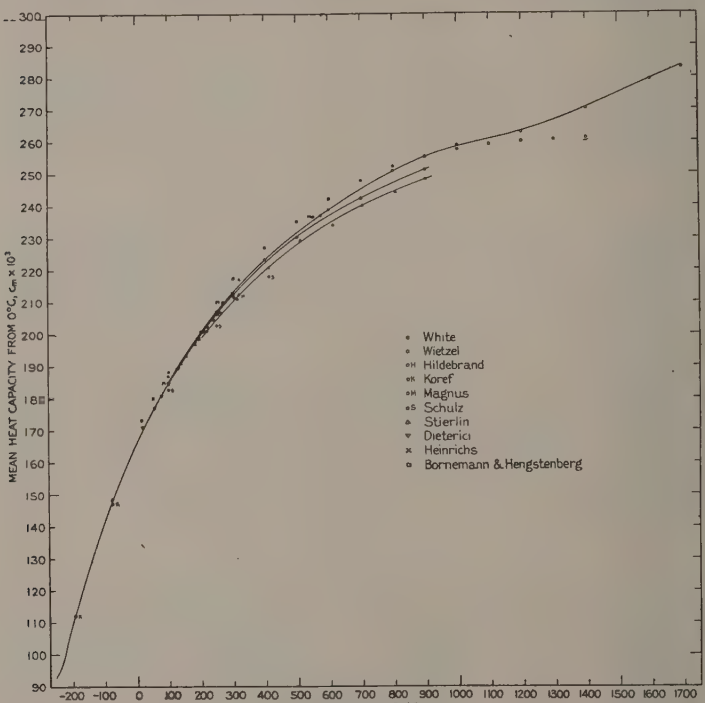


FIG. XIX.9.—Experimental data on the mean heat capacity from 0°C, for vitreous silica.

Berlin. They made 29 measurements at 13 temperatures from 100 to 1400°, using the transfer method, with an aluminum block calorimeter cooled to an initial temperature near 0°C.

Wüst, Meuthen & Durrer[51] determined the mean heat of vitreous silica[52] at 100° intervals from 100 to 1500°C, as a correction factor in their series

[50] BORNEMANN, K., & HENGSTENBERG, O., Metall u. Erz (1920), **17**: 313-319, 339-349.

[51] WÜST, F., MEUTHEN, A., & DURRER, R., Forschungsarb. Ver. Deutsch. Ingenieure (1918), No. **204**, 63 pp.

[52] Referred to throughout the publication as "Quarz." The authors even remark on the absence of "the heat-effect in the neighborhood of 580° observed by other investigators."

of measurements of the heat capacities of certain metals. They used the transfer method, with a vacuum ice-calorimeter. The material was opaque vitreous silica from the Deutsche Quarzgesellschaft. Since the specimens of glass were small (1.5 and 2 grams) and the irregular variations were of the order of 1 per cent, the precision is less than that of the other data already discussed, and I have not included the results in Figure XIX.8.

The results of Lashchenko,[53] like those of Dieterici, were obtained incidentally to another investigation, in this case a study of the heat capacity and polymorphism of zinc. The data are very irregular and apparently not of high precision, and the values at the lower and upper limits of the temperature range of 160 to 990°C depart widely from practically all other determinations. Without some additional confirmation or some explanation of the discrepancies I hesitate to give them any weight in comparison with the other available data.

The data on chalcedony

The only data on the heat capacity of chalcedony are those of Wietzel [54] and of Cohn. Wietzel's data (see Table XIX.8) form the basis for the curve in Figure XIX.10. The relation of the heat of chalcedony to that of the better-known forms is not so clear as the relations between the latent heats. Wietzel's statement that the heat-capacity curve shows a sharply marked maximum at 575° is not a necessary deduction from his published data. A less sharply marked maximum 25° lower would fit the data equally well. A maximum evidently exists, however, suggesting an inversion in chalcedony somewhere between 550° and 573°, of the same character as that in quartz at 573°. Additional measurements on chalcedony at closer intervals, especially between 500 and 600°C, are desirable.

Lashchenko [55] has published determinations of the mean heat of "chalcedony" for temperatures from 139 to 950°C. The curve of heat content shows very clearly the cristobalite inversion at 220-230°. No statement is made about the source or previous treatment of the chalcedony. If the measurements at the higher temperatures were made first, it is probable that the chalcedony was converted into cristobalite and that most of the data are really heat capacities of cristobalite. Preliminary ignition to dry the specimen might have had the same result. But if the low-temperature heat data were really obtained on fresh unheated chalcedony, then Lashchenko's specimen was very different in constitution from the chalcedony specimens studied by Washburn & Navias and by Wietzel. Under the circumstances, we can not make much use of Lashchenko's data.

The wide divergence of Cohn's values for chalcedony from those for the other forms of silica (see Table XIX.10) may have been due to the difference in thermal conductivity arising from the micro-fibrous structure. They can not be accepted without further confirmation by a different method.

[53] Lashchenko, P. N., Journ. Russian Phys.-Chem. Soc. (1913) **45**: 552-557; Ann. Inst. Polytechn. Don (1914) **3**: 1-60.
[54] Wietzel, R., article cited in note [2].
[55] Lashchenko, P. N., article cited in note [40].

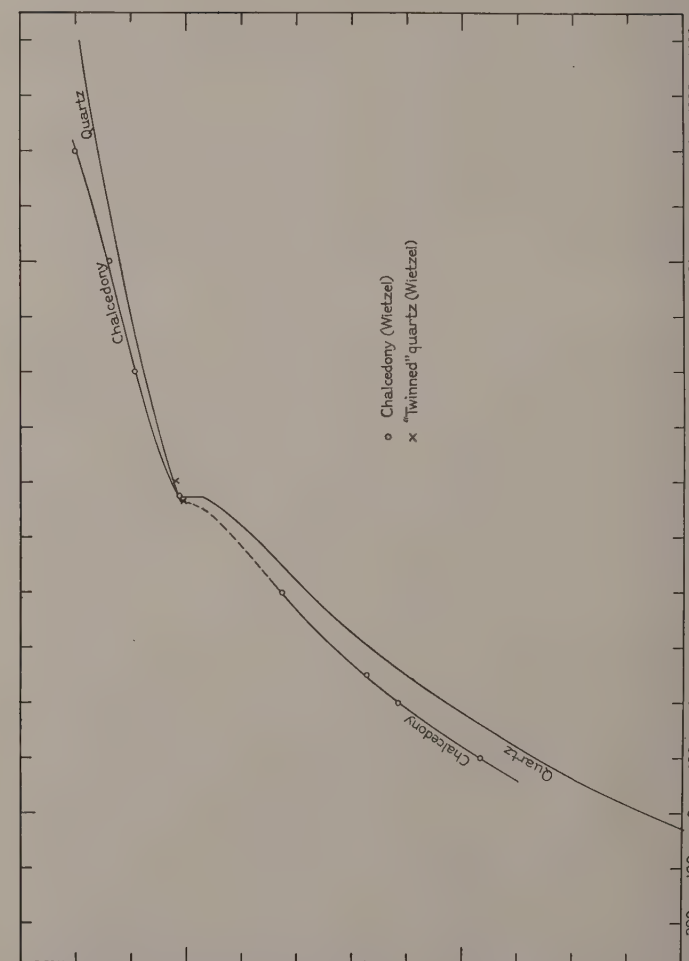


FIG. XIX.10.—Experimental data on the mean heat capacity from 0°C, for chalcedony, compared with the curve for quartz. (Figure XIX.5.)

The data on micro-amorphous silica

Cohn ran a series of measurements on amorphous silica made by heating "silicic acid" at 700° (see Table XIX.10). The data are fairly regular, and the mean heat capacity lies uniformly about 8 to 9 per cent higher than that of vitreous silica. This difference is in the direction to be expected because of the state of fine subdivision of the micro-amorphous silica, but in view of the large effect which a variation in thermal conductivity may have in Cohn's method (see p. 333), and also in view of his abnormal results with chalcedony, exact quantitative values can hardly be adopted without further measurements.

Effect of fine subdivision on heat capacity

We have seen at p. 322 that fine subdivision has an effect upon the latent heats. The degree of subdivision should affect the heat capacity also. Direct evidence on this point is offered by Wietzel,[56] who obtained the following data on the mean heat from 0° of quartz which had been finely pulverized by heating and cooling ("geglüht"):

t in °C	Quenched	Not quenched spec. (1)*	Not quenched spec. (2)*
565	0.2503	0.2472	0.2467
600	0.2523	0.2533	0.2555

* From Table XIX.8.

Unfortunately, these measurements are insufficient to throw much light on the question. As may be seen from Figure XIX.10 in which the two points are plotted, the mean heat of the quenched quartz at 565° is distinctly higher than that of coarsely-crystalline quartz at 565°, but the temperature is only 8° below the high-low inversion, and the two measurements given above may be readily interpreted as being points on the curve of a specimen of finely-divided high-quartz with an inversion temperature which has been lowered a little by the fine subdivision, thus bringing the 565° measurement within the range of the high-modification instead of the low. Furthermore, its heat at 565° differs from that of two specimens of coarse quartz by an amount only 50 per cent more than the two coarse specimens differ from each other at 500°, so the result is not very positive. What is needed is the heat capacity of coarse and very fine fractions of the same specimen of quartz at temperatures between 100 and 500°.

Stierlin[57] obtained the following rather surprising series of heat capacities by repeated determinations on the same specimen of quartz, source not stated. (I have calculated the second column using an approximate correction, calculated from that used by White, on the assumption of parallel curves.)

[56] Article cited in note [2].
[57] Article cited in XVIII, note [18].

	Mean heat	
	20° to 138°C	0° to 138°C
First determination	0.177	0.174
Second "	0.188	0.185
Third "	0.200	0.1963
Fourth "	0.2015	0.1978
Fifth "	0.2034	0.1997
Sixth "	0.2033	0.1996

The fragment weighed about 9 grams, and the heat content was determined by dropping the piece into water in the calorimeter. The sudden cooling caused the formation of a mass of fine cracks, increasing in number with successive quenchings, so that after the third determination the originally transparent quartz was milk-white and opaque. When crushed, after the sixth test, the smallest fragments still appeared white.

I am not sure just how this experiment is to be interpreted. Stierlin suggests that the work of breaking up the crystal absorbed part of the heat which would normally have gone into the water, thus making the heat capacity appear too low. The final, constant value would then be the best value for the specific heat *of finely-divided quartz*, while the best value for coarsely crystalline quartz would appear to be undeterminable from this series of measurements, excepting that it must lie between the two limits of 0.174 and 0.1996.

Comparison with the results of other observers shows that their average value is about 0.193, somewhat above the median point of Stierlin's series of six. The maximum of Stierlin's series is about 1 per cent below Wietzel's curve for chalcedony.

These facts, then, are in agreement with Stierlin's hypothesis that the work of breaking up the crystal absorbs heat, and with Wietzel's hypothesis [58] that chalcedony is only a finely divided form of quartz.

Nevertheless, in the absence of any detailed description of these experiments by Stierlin or of any confirmatory data for his interpretation of the facts his hypothesis, just referred to, cannot be regarded as satisfactory. A few per cent of firmly held water absorbed into the cracks of the quartz specimen during the quenching would account for the apparent rise in heat capacity.

The earliest attempt to determine experimentally the effect of size of grain on heat capacity of quartz was made by Ulrich [59] in 1894, who determined the heat of quartz sand, sifted to various sizes from 0.1 mm up to 2.0 mm, for the approximate interval 19 to 98°. No difference greater than the experimental error was observed, but the precision was rather low and the experiments were not capable of revealing with certainty a difference of less than about 2 per cent. The general mean of 40 determinations calculates to 0.1873 for the interval 0 to 98°.

[58] p. 84 of article cited in note [2].
[59] Ulrich, R., Wollny's Forsch. Gebiet Agrikultur-Physik (1894) **17**: 1-31.

Cristobalite

Wietzel ascribes the variation in the inversion-point of cristobalite with its temperature of formation (first noted and described by Fenner, see VII) to a difference in the degree of fineness or degree of twinning, or both combined. He found that the heat of inversion of 1100°-cristobalite was notably smaller than that of 1600°-cristobalite, and also that the maximum of heat capacity at the inversion was less sharply marked in 1100°-cristobalite than in the 1600° variety. Both facts support his hypothesis.

Fenner also considered this hypothesis and made a careful series of experiments on the effect of fineness of grain on the inversion-point, which I believe satisfactorily disposed of the hypothesis. He found the maximum effect to be only a few degrees, while the differences to be accounted for are of the order of magnitude of 50° (see IX).

Variation in the assumed size of twinned regions, as affected by the rate of cooling through the inversion-point (see p. 144) was also studied experimentally by Fenner, and the effect found to be only about 1°.

Twinning

In preceding pages we have considered the effects of fine mechanical subdivision on latent heats and heat capacities. There remains another very important structural variation which is presumably equivalent to fine subdivision, namely, twinning.

Unfortunately there is no direct experimental evidence of the effect of twinning upon the thermal properties. There is a certain amount of inference, assuming the existence of twinning without definite optical proof of its presence, but this is hardly sufficient.

Relation of heat capacity to temperature

The true heat capacity of all substances yet investigated becomes very small at very low temperatures, apparently approaching zero as the temperature falls.

At very high temperatures, not too near the melting-point, the true heat approaches a constant value, approximately inversely proportional to the atomic weight if the substance is a chemical element, or to the average atomic weight if the substance is a compound.

Between these two extremes the curve of heat capacity against temperature shows a steeply rising portion, with an inflection in curvature. The temperature of this steeper portion varies considerably with different substances. The curves for the forms of silica are so placed that room temperatures lie within the range of the steeply rising portion; hence their heats at 20°C are comparatively low, and increase rapidly with temperature.

The true specific heat at constant volume, c_v, for most solid substances, has been found to be proportional to T^3, the cube of the absolute temperature, at very low temperatures. The true specific heat at constant pres-

sure, c_p, which is the one obtained experimentally, is only a few per cent greater than c_v, and therefore c_p also is approximately proportional to T^3.

None of the data on silica appear to reach low enough temperatures to come under this T^3 law. The data on vitreous silica go lowest, namely, to 18.9°K, but c_p is closely proportional to T^2 from 18.9 to 27°K, instead of being proportional to T^3. This will be evident from the curve in Figure XIX.3.

The theoretical significance of the T^3 and T^2 laws will be discussed in a later section.

Relation of heat constants to volume

Wietzel points out that the differences in heat content between quartz and vitreous silica, and cristobalite and vitreous, respectively, as found by him are in the same ratio as the differences in density:

	Difference in density from vitreous	Difference in heat content from vitreous
Quartz	2.65 — 2.21 = 0.44	2.33
Cristobalite	2.32 — 2.21 = 0.11	0.57
Ratio	4.0	4.1

In 1904 Richarz suggested an empirical rule connecting specific volume and heat capacity, to the effect that if there are two modifications of a substance, the one with the greater specific volume has also the greater heat capacity. The rule fails for vitreous silica versus quartz from about 0 to 573°C, for vitreous versus cristobalite from — 175 to 250°C, and for cristobalite versus quartz from about 250 to 573°C. In other words, Richarz's rule ceases to be applicable in the same region where van't Hoff's rule of the relation of stability to heat capacity would fail, namely, where the high-low inversions are preceded by a "distributed latent heat" (p. 310) or abnormal increase of heat capacity.

Richarz's rule applies to cristobalite versus quartz in the range — 253 to — 180°C, where data are available. Wietzel has attempted to apply it quantitatively to this pair, stating that c_p for cristobalite is about 20 per cent higher than c_p for quartz, while the volume at atmospheric temperatures is also about 20 per cent above that of quartz. An inspection of Figure XIX.3, however, will show that anything more than a qualitative generalization is hardly justified by the data.

The thermodynamic constants of silica

Entropy and energy

The *First Law of thermodynamics* states that when energy disappears at one place an equal amount of energy appears at a neighboring place; the total amount remains constant.

The *Second Law of thermodynamics* states that heat will, of itself, flow only from a warmer body to a colder body, never in the reverse direction.

These laws are the result of experience; that is, they are a concise formulation, in agreed-upon terms, of the results of a great abundance and variety of observations and experiments. The concept of the flow of something permanent, called "heat," in only one direction, as expressed in the Second Law, introduces a kind of quantity into physics which is different from length, mass, time, and electric charge. Clausius named it *entropy,* Tolman calls it "degree of run-down-ness"; or we might give it other names indicating its usefulness as a quantitative measure of the energy which is continually becoming unavailable, and expressive of the idea that the universe as a whole appears to us as if it has been wound up and is now going irretrievably towards some distant condition of inactivity or dead level.

Not knowing where that dead level is, we can not measure the absolute value of entropy, but only the *change of entropy* in any process, such as the formation of quartz out of silicon and oxygen at 0°C. This change is given a quantitative definition by being related to energy and temperature thus: $dS = dQ/T$. This states that the absorption of the infinitesimal quantity of heat energy dQ, in a reversible process, at the temperature T, increases the entropy of a system by the infinitesimal quantity dS. The quantity $T dS$ thus resembles the quantity $p dv$; temperature is the pressure factor of heat energy and entropy is its volume.

Measurement of entropy and energy

The entropy of 1 gram of a substance under stated conditions is a constant, characteristic of the substance. Hence the difference of its entropy from that of some standard substance under standard conditions is also a characteristic constant, and it is this difference that is always meant by the term "entropy" when it is given a numerical value. In steam tables, for instance, it is convenient to take the entropy of water at 0°C and 1 atmosphere pressure as the zero of reference.

If we knew the entropy-changes in the conversion of the chemical elements one into another, we could, for example, adopt the entropy of hydrogen at 0°C and 1 atmosphere as our arbitrary zero for all substances. But since the transmutation of the elements is not yet an important reaction in every-day chemistry, it is convenient to call the entropy of some specified modification of each of the elements zero at 0°C and 1 atmosphere. The numerical value of the entropy of every substance at every temperature and pressure is thereby fixed, because the change of entropy in synthesizing any substance from its elements can be measured experimentally, and the change of entropy with temperature and pressure can also be measured experimentally.

We know little about the possible stores of *energy* within the atoms and molecules. Just as with entropy, we can only measure differences (but see also p. 349). Again it is convenient to take the energy of a specified modification of each chemical element as zero at 0°C and 1 atmosphere pressure.

A table of the energies and entropies of a substance, measured from such a zero, at various temperatures and pressures, condenses a great deal of useful information into a small space.

We are not restricted to the tabulation of energy and entropy only. Any two unequivocally defined derivatives of the two will do equally well, as will appear below.

Formulation of the two laws

A combination of the First and Second Laws is contained in the equation: $dU = TdS - dW$. This equation states that in a reversible process the differential of the total energy of a system is equal to the absolute temperature multiplied by the differential of the entropy of the system, less the differential quantity of work done by the system on its surroundings. If only mechanical work is considered, dW is replaced by pdv: $dU = TdS - pdv$. Many of the important relations of thermodynamics are derived from this equation.

There are three functions derivable from the fundamental equation which are particularly useful and important. They are:

$D_1 = U + pv$, originally called the *heat-content;*
$D_2 = U - TS$, originally called the *free energy* (but see below);
$D_3 = U - TS + pv$, originally called the *thermodynamic potential.*

Like entropy and energy, each of these three quantities D_1, D_2, and D_3 —call them by whatever names you prefer—may be looked upon as having an absolute value which remains unknown to us, but of which the change during a given process, such as the formation of quartz out of silicon and oxygen at 0°C and 1 atmosphere pressure, can be determined. The adoption of zero levels for energy and entropy fixes the zero levels for these derived quantities also.

The first of the three, the heat-content, usually represented by H, is useful because it contains the ordinary heat of reaction. The second of the three is useful because the amount by which it changes in any isothermal process is the maximum outside work which can be obtained from that process. Its quantitative measure is usually represented by A.

The third quantity, D_3, is useful because the amount by which it changes in any isothermal process is the maximum non-mechanical work which can be obtained from the process under such practical circumstances as, for example, control the output of a galvanic battery. When the change of pv is small, D_3 differs very little from D_2.

D_3 is particularly useful because the direction in which it changes in a given reaction at constant temperature and pressure determines whether that reaction proceeds spontaneously or not. If D_3 decreases, the reaction proceeds. It is thus a test of the *stability* of a system; if the system is a pure substance, such as silica, D_3 determines the stability of its polymorphous forms and its states of aggregation (see Chap. IV).

The greater practical usefulness of D_3, as compared with D_2, in physicochemical calculations has caused G. N. Lewis, and many American chemists following his example, to call D_3 the "free energy." This has caused confusion because Helmholtz and others had already called D_2 the free energy. I propose to call it simply the *zeta*, after the Greek letter which Gibbs employed to represent the function.[60] Following Lewis' notation, its numerical value will be represented by F.

Thermodynamic tables for silica

This is the place to introduce complete tables of the energy, entropy, and zeta of pure silica in all of its forms. Unfortunately the heat of combination of silicon with oxygen, and the heat capacity of silicon itself, are known only to the roughest approximation. The data on heat capacities of quartz and vitreous silica, presented earlier in this chapter, are fairly good, but cristobalite is dubious and so are the heats of fusion and inversion of the two forms mentioned, while on tridymite there is no information at all. The thermodynamic tables will therefore have to wait for more and better data.

The qualitative relations among the zetas of the various modifications are fairly represented in Figures IV.2 to IV.5.

Silica and the Third Law of thermodynamics

In the preceding discussion we have adhered strictly to a temperature of 0°C and a pressure of 1 atmosphere as the standard conditions under which the chemical elements are assigned zero entropy and energy. These conditions are particularly desirable as a basis for experimental constants because they are easily reproduced whenever new or more accurate or more precise energy and entropy data are wanted.

Some useful simplifications are introduced, however, if we change the standard temperature for zero entropy and energy from 0°C to 0°K, the

[60] This term is to be preferred for the following reasons: (1) so important a quantity, one which will have to be increasingly used not only in science but in industry, needs a single-word expression, for a two-word name always tends to shorten itself (see p. 43 for a striking example); (2) the proposed name is short, easy to remember, spell, and pronounce; (3) it is not burdened with the troublesome and misleading connotations which go with familiar English words like "free" and "energy"; (4) it is in accordance with the rule of priority, because J. Willard Gibbs first showed its importance in chemistry and its relation to energy and entropy; he represented it by the symbol ζ. His alternative name of "thermodynamic potential" is altogether too ponderous.

"absolute" zero. But as this zero will always be experimentally inaccessible, data based upon it must be held open for theoretical revision to an extent which is not necessary at 0°C.

A simplification in the energy and entropy relations of substances at the absolute zero was foreshadowed by Le Chatelier, G. N. Lewis, Richards, Haber, and others, but was first clearly formulated by Nernst. The principle, now generally known as the *Third Law of thermodynamics,* states that: "In an isothermal process involving only pure solids and liquids, the entropy-change approaches zero as the temperature approaches zero."

If the entropy of each element is taken as zero at 0°K, this evidently means that "the entropy of every chemically homogeneous liquid or solid substance is zero at 0°K." Lewis and Gibson have modified this statement, showing that the entropy of liquids may depart from the law, and suggesting this form: "If the entropy of each element in some crystalline form be taken as zero at the absolute zero, the entropy of any pure crystal at the absolute zero is zero, and the entropy of any other substance is greater than zero."

It is evident that the Third Law may not be applicable to vitreous silica. If the entropy of a substance be interpreted as a measure of the probability of occurrence of its own particular configuration of atoms or molecules, we may perceive a reason why the entropy of a glass should depart from zero at 0°K. In a crystalline substance there is no factor of chance in the arrangement of the atoms when thermal vibration has ceased. But in a glass there is disorder in the arrangement, and many arrangements are possible, so that there is a measurable variation from the most probable and hence a measurable entropy.

If the hypothesis of the structure of cristobalite presented in Chapter XV (p. 258) proves to be correct, cristobalite will also be an exception to the Third Law, and a minor modification will be necessary in Lewis & Gibson's form of that law. According to the hypothesis, cristobalite contains a variable proportion of unordered oxygen atoms within a structure which is, as a whole, orderly, that is, crystalline. The proportion of unarranged oxygen atoms varies with the temperature of formation of the cristobalite. But the existence of randomness means, just as with a glass, that the entropy at 0°K is not zero. Furthermore, not only would the entropy at 0°K differ from zero, but its value would vary with the original temperature of formation of the cristobalite.

Relation of heat capacity to stability

In 1904 van't Hoff [61] proposed an empirical rule relating heat capacity and stability, to the effect that if a substance occurs in two modifications, the one which is stable at the higher temperature has the higher heat

[61] van't Hoff, *Boltzmann Festschrift* (1904, Leipzig), p. 233.

capacity. It is now evident that this rule is a qualitative corollary of the Third Law.

The rule is true for silica only at very high and very low temperatures. Through a range of intermediate temperatures (about 0 to 573°C for quartz and —175 to 350°C for cristobalite) the heat of vitreous silica is clearly lower than that of quartz and cristobalite, whereas if the rule held at all temperatures it should be higher. Similarly, the heat of cristobalite is lower than that of quartz from about 250 to 573°C, although according to the rule it should be higher.

These reversals of van't Hoff's rule are evidently caused by the "distributed latent heat" (see p. 310) of inversions in quartz and cristobalite at the upper limits of the temperature-range of reversal, but they show that the rule is not of general application. It must be restricted to substances whose modifications remain alike in constitution over the whole range considered. As the temperature- and pressure-ranges of experimentation are widened, examples of such substances are likely to become less and less numerous.

Theory of the heat capacities and latent heats of silica

Heat capacity in general

For purposes of comparison and theory, the *atomic heat* is much more convenient than the true heat capacity, which is based upon 1 gram. If the substance is an element, the atomic heat is simply the true heat multiplied by the atomic weight. For a compound, the *average atomic heat* is defined as the true heat times the formula weight divided by the number of atoms in the formula. For silica, the average atomic heat at constant pressure, C_p, is: $C_p = c_p \times \frac{60.06}{3} = 20.02\ c_p$, if c_p is the true heat at constant pressure. Correspondingly, the average atomic heat at constant volume, $C_v = 20.02\ c_v$. This is simply a definition, involving no assumption or theory regarding the individual part played by each atom in determining the heat capacity.

When heat energy is put into a solid substance, such as silica, to raise its temperature, the energy may be looked upon as distributed in the following ways:

(1) A large proportion goes to increase the kinetic energy of the vibrating units of the solid.
(2) Another large proportion goes to increase the mutual potential energy of the vibrating units, because their kinetic energy has been increased.
(3) A widely varying proportion may be stored as "distributed latent heat" (see p. 310) due to intra-atomic or intra-molecular changes.
(4) A relatively small proportion goes into expanding the solid against the internal cohesion of the units.
(5) A very small proportion does work against the external pressure.

The vibrating units, which take most of the energy, may be atoms or atom-groups, or both. Assuming, for illustration only, the theory of silica structures given in Chapter XV, we find that kinetic and potential energy are taken up

(a) by silicon and oxygen atoms vibrating individually
(b) by SiO_2 atom-triplets vibrating as units
(c) by silica threads vibrating as units.

If the energy of these vibrating units were calculable from the classical kinetic theory, the true heat capacity of silica would be nearly constant, and would have a value of about 6 gram-calories per 60.06 grams. This is roughly true at high temperatures, but at low temperatures the true heat, as we have seen, becomes very small, actually approaching zero.

The *quantum theory of energy,* advanced by Planck, explains this falling off. It assumes that energy can only be taken up by the vibrating units in definite quanta of the size hν, in which h is a universal constant of matter and ν is a characteristic frequency of vibration of the unit in question. Einstein applied the theory to solid substances and deduced his well-known formula for true atomic heat at constant volume:

$$C_v = 3R \frac{e^{\frac{h\nu}{kT}} \left(\frac{h\nu}{kT}\right)^2}{\left(e^{\frac{h\nu}{kT}} - 1\right)^2}$$

in which R is the familiar gas-constant, 1.987 calories per degree; e is the base of natural logarithms; h and k are universal constants; and T is the absolute temperature.

By cutting and trying, we get the most favorable value of the quantity $\frac{h\nu}{k}$, which we may consider for the moment as a characteristic constant of the substance to be deduced from its heat-capacity data as a whole. The Einstein formula can thus be made to fit the larger part of the heat curve, but no value of $\frac{h\nu}{k}$ will make it fit the main portion and the very low-temperature portion at the same time. The formula drops to zero too rapidly.

Nernst & Lindemann made a purely empirical addition to Einstein's formula, by adding on a term containing $\frac{1}{2} \cdot \frac{h\nu}{kT}$ in place of $\frac{h\nu}{kT}$, and this fits the data very much better (changing $\frac{h\nu}{k}$ somewhat at the same time), but we shall not be further concerned with this formula, since a still further improvement has been made by Debye.

Debye's formula is a step in advance over Einstein's, in its success in

representing the entire heat-capacity curve. Treating the solid mathematically as if it were continuous, and applying the quantum theory as Einstein did, Debye developed the following formula for the total energy per gram-atom:

$$U = \frac{9R}{\nu_m^3} \int_0^{\nu_m} \frac{\frac{h\nu^3}{k}}{e^{\frac{h\nu}{kT}} - 1} d\nu$$

This may be developed into a series, to make a workable formula for atomic heat at constant volume, which need not be given here.

The Debye formula fits the high-temperature heat capacities just as well as the Einstein formula, and fits the low-temperature data very much better. It is not perfect, however. The Einstein curve approached zero much too fast, but the Debye curve approaches zero just a little too slowly for some substances. The actual experimental curve is in between, though usually closer to the Debye curve than to that of Einstein.

The reason for this is probably to be found in the following considerations. Einstein's formula assumes units vibrating individually, all with the same frequency ν. Debye's formula contains a frequency ν_m which, as Nernst says, is a "physically-speaking undefinable" frequency but may be regarded as an upper limit to a range of frequencies of individually vibrating units, this upper limit being characteristic of the unit. Now suppose that not only do all the atoms vibrate individually, but some proportion of them vibrate as pairs, another smaller proportion as triplets, another still smaller proportion as sextets, and so on. Then the total number of vibrating units is in reality greater than was assumed for the Einstein formula, and that is why the C_v of that formula was too low. The Debye formula, in effect, took care of this unknown number of pairs, triplets, etc., by assuming a whole series of slower ν's, increasing to and culminating in that of the atom, but overdid it mathematically through lack of exact knowledge of just how the numbers of pairs, etc., were really distributed.

The preceding considerations on the heat capacity of a solid are based on somewhat crudely simplified assumptions regarding its constitution. What we are really dealing with in a solid is not a collection of isotropic atoms all vibrating alike (Einstein formula), nor a collection of atoms vibrating in a variety of groupings (Debye and other modified formulas), but a complex *structure* of atoms and atom-groups in which the vibrating unit with the characteristic ν has a position and an orientation as well as a number. This has been well brought out by Born & Karman.[62] Their general formulation reduces by approximations in particular cases to a summation of Debye and Einstein functions, indicating the reason for the

[62] Born, M., & Karman, Th. v., *Zur Theorie der spezifischen Wärme*, Physikal. Zeitschr. (1913) **14**: 15-19. See also Born, M., *Dynamik der Kristallgitter* (1915, Leipzig), p. 72-77.

partial success of each of those functions in the cases to which they were first applied. Although these more complete formulas of Born have not been tested rigorously by experimental data, they evidently contain the material for a more thorough theoretical treatment of heat capacities than has yet been available.

From another point of view, the approximate formula of Born containing both Einstein and Debye terms may be looked upon as a purely empirical resort. Since the Einstein formula falls too fast, and the Debye formula too slow, it is evident that a judicious mixture of the two, or of several Debye and several Einstein formulas with different ν's, can be made to fit almost any heat curve. In fact, such a combination was suggested by Nernst as an empirical interpolation-formula.

At very low temperatures Debye's formula reduces to the simple form:

$$C_v = \frac{12}{5}\pi^4 R\left(\frac{kT}{h\nu}\right)^3; \quad \text{that is, } C_v = \text{Const.} \times T^3.$$

The range within which this simple form is equivalent, within reasonable limits, to the more complex form depends, of course, on ν as well as on T. The limit may be set practically at values of ν and T such that $\frac{h\nu}{kT} = 10$, which is equivalent to $C_v =$ about 0.46.

Applications to the heat capacity of silica

Simon [63] has shown that the heat capacities of several widely differing organic compounds follow a similar course at low temperatures. They are linear over a considerable range of temperature, and reach the T^3 region only at very low temperatures, lower than those characteristic of the metals, for example. The course of the curve is also best expressed by a sum of Debye formulas, without any Einstein term.

Simon further points out that a curve of heat capacity similar to that just described may be expected from substances which contain a considerable number of bonds with which high vibration-frequencies may be associated; that is, substances which have a small average atomic weight and a large number of atoms in the molecule, or which polymerize.

Silica appears to come under this classification. The average atomic weight of its atoms is about 20, which, though not so low as the organic substances, is much lower than most metallic compounds. I have already indicated reasons for believing that its atoms are combined into triplets, and these associated into threads; that is, it is an associated or polymerized substance.

The low-temperature heat-capacity curves of silica, as far as they go, are in full accord with this classification. Its average atomic heat is much lower than that of its analogous compound in the same group, CO_2, whose properties indicate that it is not polymerized. Furthermore, as has been re-

[63] Article cited in note [25].

marked above, the data for many substances fit the "T^3 law" very closely; the data on the modifications of silica, however, do not fit such a curve. The heat of vitreous silica, which has been carried the furthest (down to 18.9°K), is varying between that temperature and 29°K proportionally to T^2 instead of T^3.

Simon offers the following explanation of this failure to follow the T^3 law. The limit of applicability of the formula $C_v = \text{const.} \times T^3$ depends, as already noted, on the value of ν. If the mean atomic heat is the result of a sum of several Debye functions, each with its own value of ν, the one with the smallest ν will be the first, with rising temperature, to reach its T^3 limit, and that part of the atomic heat due to it will then

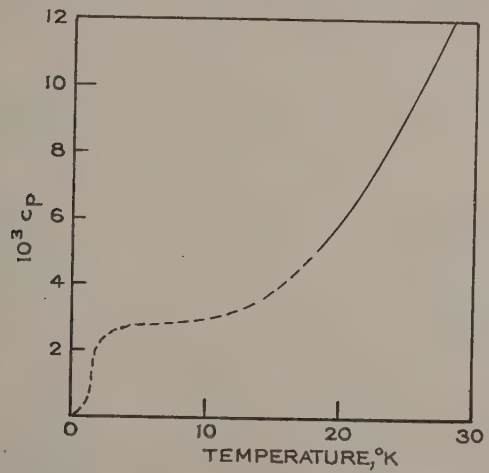


FIG. XIX.11.—Possible form of the curve of true heat capacity for vitreous silica near 0°K.

increase less rapidly than T^3. But if the other characteristic ν's in the sum are relatively much larger than this first one, their contribution to the total will be very small, and although they will still be within the T^3 validity-range for their ν's, they will not be able to counteract the falling away from T^3 due to the first item.

Now polymerized substances are just the ones in which relatively low characteristic ν values may be expected to be found, due to heavy vibrating units or weak constraints, along with larger ν's due to smaller units (small atom-groups, and individual atoms). Hence the departure of silica from the T^3 law.

The heats of quartz and vitreous silica at low temperatures indicate that the silicon and oxygen atoms have different frequencies, as do the atoms in AgCl, HgCl, C_6H_6, and various other compounds. This is one

respect in which silica differs from the salts KCl, NaCl, and KBr, in which both kinds of atoms have approximately the same frequency.

Possible form of heat-capacity curves of silica below 20°K

Some indications as to the course of the heat curves of silica from 19° down toward 0°K can be had from the melting-points. Suppose the curve for vitreous silica to be extrapolated in the simplest geometrical way, and a T^3 law to be assumed for quartz and cristobalite.[64] With these completed heat curves and the heats of crystallization as a basis, curves of the change of heat content, ΔH, against T for the reactions quartz ⇄ vitreous and

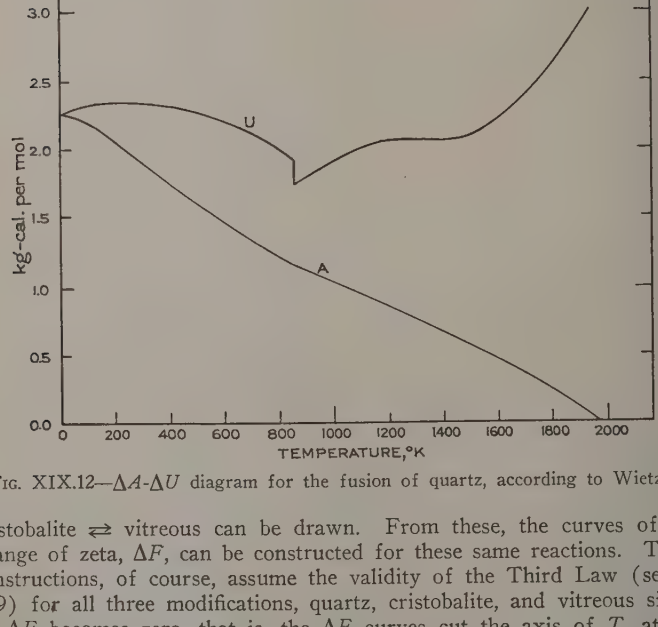


Fig. XIX.12—ΔA-ΔU diagram for the fusion of quartz, according to Wietzel.

cristobalite ⇄ vitreous can be drawn. From these, the curves of the change of zeta, ΔF, can be constructed for these same reactions. These constructions, of course, assume the validity of the Third Law (see p. 349) for all three modifications, quartz, cristobalite, and vitreous silica.

ΔF becomes zero, that is, the ΔF curves cut the axis of T, at the melting-points. In this manner a melting-point of 2300°C. is obtained for quartz, and of 4000°C for cristobalite. These are far above the experimentally determined melting-points. The discrepancy, then, is probably due to wrong assumptions regarding the heat capacities below 28°K, espe-

[64] Wietzel, R., article cited in note [2].

cially since the course of the ΔF curve is mainly determined by the values at very low temperatures.

Assuming that the T^3 law for quartz and cristobalite is correct, and that all three follow the Third Law, how must the heat curve of vitreous silica be modified in order to draw back the ΔF curves and make them intersect the T-axis at the experimentally determined melting-points of quartz and cristobalite? A modification such as that shown in Figure XIX.11 would accomplish the purpose. The upper end of the T^3 region for vitreous silica would be brought down to the neighborhood of 5°K.

The uncertainty about the course of the heat-capacity curve for vitreous silica below 20°K makes it impossible to construct exact curves of ΔF and ΔH for the reaction quartz $\rightleftarrows$ vitreous or cristobalite $\rightleftarrows$ vitreous. A tentative diagram is given by Wietzel (using ΔA and ΔU in place of ΔF and ΔH,—but the difference is very slight) and is reproduced in Figure XIX.12. It is based on a melting point for quartz of about 1700°C and an assumed heat curve for vitreous silica like that in Figure XIX.11. The assumed melting-point is too high (see p. 89) but the form of the curve may be qualitatively correct.

Analogy with silicate glasses

Wietzel [65] has pointed out the analogies between vitreous silica and the glasses of orthoclase ($K_2Al_2Si_2O_8$) and lithium beryllium borate. The melting-point of orthoclase, when estimated with the aid of the ΔU and ΔA curves, comes out 4000°C as compared with 1200° experimentally determined. The discrepancy is best explained, just as with quartz and cristobalite, by assuming an abnormal heat curve at very low temperatures, and a very low T^3 region. Lithium beryllium borate glass has been studied at very low temperatures, and its T^3 region found to be below the lowest temperature of measurement.

As a theoretical explanation Wietzel suggests that the amorphous glassy solids in general contain a certain limited number of loosely bound atoms, whose atomic heat, like that of a gas, does not fall off rapidly until the very lowest temperatures are reached. This assumption is entirely consistent with the theory of structure of silica set forth in Chapter XV and elaborated in later chapters. The loosely bound atoms are those atoms of oxygen whose freedom permits them to play the principal part in the phenomena of annealing and anomalous birefringence.

An inversion below 20°K?

The assumed form of heat-capacity curve for vitreous silica below 20°K suggests an inversion-point, which might be similar to the high-low inversions in the crystalline modifications. The existence of such an inversion would be consistent with the general theory of structure set forth in

[65] Article cited.

Chapter XV. In fact, such an inversion at low temperatures had been predicted as one possible consequence from the theory, but other considerations seem to make more probable the alternative possibility that the inversion is spread out over a range of temperatures. If it should turn out that there is an inversion in vitreous silica below 20°K, then the hypotheses regarding the structure of the glass will need to be modified in certain particulars, although the theory as a whole would not be changed.

Heat capacity at high temperatures

The more rapidly rising portion of the heat curve of vitreous silica, beginning at about 1300°, may be connected with the beginning of softening of the glass. It is analogous to the much more sharply marked changes in amorphous glycerol [66] at about —100°C and amorphous alcohol [67] at about —180°.

As White [68] has pointed out, the heat-capacity curve for vitreous silica begins as far down as 600°C to rise above the theoretical limiting value. Further, if allowance were made for the negative thermal dilatation of quartz above 573°, and for the small and possibly negative dilatation of cristobalite at similar temperatures, it appears likely that both of these forms, also, would have heat capacities above the theoretical.

Theoretical calculation of the latent heat of fusion

The latent heat of fusion of a substance is theoretically related to the lowering of its freezing point produced by the dissolving in it of a second substance to form an "ideal solution." Washburn [69] has applied this relation in the form: $L = \frac{RT^2}{\Delta T} x_1$ to the lowering of freezing point of cristobalite by the addition of Al_2O_3. L is the latent heat of fusion at 1710°C, R is the gas constant, T the absolute temperature of melting of cristobalite, ΔT the lowering of melting-point, and x_1 the mol fraction of the added substance. The temperature and composition of the eutectic between SiO_2 and the most siliceous compound of SiO_2 and Al_2O_3 gives a point sufficiently near to pure SiO_2 to justify a calculation.

The value thus obtained by Washburn, on the assumption that the dissolved substance is Al_2SiO_5, was 6.95 kg-cal. per formula-weight SiO_2, which is far too large. Better data are now available [70] and the calculation can be revised. The composition of the eutectic is 3.3 mol per cent Al_2O_3, and ΔT is 165°. If we assume that the dissolved substance is non-associated Al_2O_3, the calculated value of L comes out 1.56 kg-cal.: if Al_2SiO_5

[66] Simon, F., article cited in note [35].
[67] Gibson, Parks, & Latimer, J. Amer. Chem. Soc. (1920) 42: 1542-1550.
[68] p. 25 of article cited in note [33].
[69] Washburn, E. W., article cited in note [12].
[70] Bowen & Greig, *The system Al_2O_3—SiO_2*, J. Amer. Ceram. Soc. (1924) 7: p. 243.

(sillimanite), the value of L is 1.63; if $3Al_2O_3.2SiO_2$, which is the only known compound of Al_2O_3 and SiO_2 which is stable at this temperature, L is 0.54 kg-cal. per formula-weight. These values are not very different from the value obtained from heats of solution (see pp. 312 and 318), but the agreement may be accidental and due to a balancing of errors. We have assumed that the liquidus from pure SiO_2 down to the eutectic is a straight line, which is probably not true; and the state of association or dissociation of the solute is quite unknown. The order of magnitude is certainly right, however.

Theory of latent heat of inversion

Perrier's theory [71] of the disappearance of a spontaneous polarization at the inversion-point would call for the disappearance of a certain quantity of heat, in other words, a latent heat of inversion. The mechanical hypothesis presented in Chapter XV would likewise require some heat energy to be stored in a potential form. The facts are qualitatively in agreement with this expectation.

It is rather surprising, however, that the relatively large volume change at the inversion-point of quartz should be accompanied by so little absorption of heat. It would seem at first sight that a large attraction between atoms would have to be overcome, and it might be expected that the amount of energy thus absorbed and converted into potential energy would be of the same order of magnitude as the heat of fusion.

In Chapter XV the general hypothesis was offered that the high-low inversion is due to a change of shape of the atom-triplet, through a change in the orbits of certain electrons. The special hypothesis suggested at p. 258 to explain this change of shape was that the vibratory oscillation of a pair of electrons is changed into a rotation. This might account for the small latent heat. The conversion of translational motion into rotatory motion releases the potential energy of the oscillation, which is half of the total energy of oscillation, and makes possible the storage of an equivalent amount of energy in the enlarging of the lattice of the structure.

[71] Article cited in VII, note [10].

Chapter XX. THERMAL CHANGES IN VOLUME AND SHAPE

We have seen in Chapter XII that each crystalline modification of a substance has a characteristic *symmetry*, and that the symmetry and axial ratios together define its characteristic *shape*. It also has a characteristic *volume*, which has been considered in Chapter XVIII.

The study of the effect of external conditions upon these three will now be in order.

Changes in symmetry

Changes in symmetry are necessarily discontinuous, and correspond to the formation of new polymorphous modifications (see VII). But in the type of inversion here called "high-low inversion" there is usually a close geometrical relationship between the high-temperature and the low-temperature modifications. It is therefore convenient to consider them together, especially with respect to their thermal properties, because the inversion is primarily dependent upon rise and fall of temperature and is readily reversible.

Changes in shape and volume

Any external condition which influences the distances apart of atomic centers may cause a change in the volume or the shape, or both. These properties are therefore affected by pressure, stress, and temperature, and may also be affected by radiation, electrification, or magnetization. The first three are the effects most frequently observed. We shall consider now the effects of changing temperature at atmospheric pressure.

Thermal changes in shape and volume

The most obvious effect of changing the temperature of a body is the change in its dimensions. This may be partly expressed as a change in volume, called the *thermal dilatation*. But this does not express the effect completely. If the substance is crystalline, it will not, in general, change to the same extent in different directions; it undergoes not only a change of volume but also a simultaneous change of shape. A sphere of quartz made spherical at atmospheric temperature will not remain a sphere if heated (or cooled), but will become flattened (or elongated), forming an ellipsoid. This change of shape is best expressed as a thermal change in the axial ratio or ratios,—there will be one or two, depending upon the symmetry (see XII). The change in axial ratios will be referred to here as the *thermal deformation*. Both dilatation and deformation may be comprised in the term *thermal expansion*.

Besides these two different aspects of the change, we must also distin-

guish the two different degrees of change which are characteristic of those substances, such as silica, which show high-low polymorphism.

There is first the continuous expansion or contraction usually expressed by means of a "coefficient," giving the amount of change in the volume or in the axial ratio per degree of temperature.

Second, there is the more or less abrupt change which each of the principal forms undergoes in changing from one modification to another, at a

TABLE XX.1.

DENSITIES AND KILOGRAM-VOLUMES OF THE MODIFICATIONS OF SILICA.

Note: The volumes and densities of tridymite and cristobalite are not known with the accuracy indicated by the values given in the Table; these indicate only *relative* values at different temperatures, on the basis of assumed values at 0°.

t °C	Quartz		Tridymite		Cristobalite		Vitreous	
	d	10^3v	d	10^3v	d	10^3v	d	10^3v
—250	2.665	375.3					2.203	454.0
—200	2.664	375.4					2.203	454.0
—150	2.662	375.7						
—100	2.659	376.1					2.203	453.9
— 50	2.655	376.7						
0	2.651	377.3	2.262	442.0	2.320	431.0	2.203	453.9
50	2.646	377.9	2.255	443.5	2.317	431.5		
100	2.641	378.7	2.249	444.7	2.313	432.4	2.203	454.0
117			⎧2.247	445.1				
			⎩2.242	446.0				
150	2.636	379.4	2.235	447.4	2.305	433.8		
163			⎧2.233	447.9				
			⎩2.228	448.8				
200	2.630	380.3	2.221	450.2	2.292	436.3	2.202	454.1
250	2.623	381.2	2.214	451.6	2.229	448.6		
300	2.616	382.2	2.209	452.7	2.222	450.0	2.202	454.1
350	2.609	383.3						
400	2.601	384.5	2.201	454.3	2.212	452.	2.202	454.2
450	2.591	385.9						
500	2.581	387.5	2.195	455.6	2.208	453.	2.201	454.3
550	2.564	390.0						
573	⎧2.554	391.6						
	⎩2.533	394.8						
600	2.533	394.8	2.192	456.3	2.203	454.	2.201	454.4
700	2.534	394.7	2.189	456.8			2.201	454.4
800	2.535	394.5	2.189	456.9			2.200	454.5
900	2.537	394.1	2.189	456.8			2.200	454.6
1000	2.541	393.6	2.190	456.6			2.200	454.6
1100	2.543	393.2					2.199	454.7
1200	2.546	392.7						

high-low inversion point. This change in dimensions is known to be the accompaniment of a change in symmetry in each of the following inversions: low-quartz to high-quartz, low-tridymite to lower high-tridymite, and low-cristobalite to high-cristobalite. It is not known whether there is a change of symmetry at the inversion of lower high-tridymite to upper

high-tridymite, although it is known that there is a sudden change of volume at this point (see also p. 124).

Thermal dilatation

Experience shows that the *rates* at which a substance changes its dimensions with changing temperature are more often characteristic constants of the substance than are its actual specific volumes at a series of temperatures. In other words, the whole volume-temperature curve of a substance may be raised or lowered appreciably, while the slope of the curve is not affected to anywhere near the same extent.

This is the justification for the usual custom of tabulating the specific volume at some standard temperature as one characteristic constant of the substance, while its departure from that standard volume when the temperature is raised or lowered is considered as another, so-called "thermal," constant.

Table XX.2.

True Coefficients of Thermal Dilatation (Volumetric) for the Modifications of Silica.

t °C	Values of $10^6\alpha$			
	Quartz	Tridymite	Cristobalite	Vitreous
—200	12.			—2.6
—150	19.			
—100	25.2			—0.9
— 50	29.8			
0	33.6	73	17	1.1
50	36.8	61	29	1.5
100	40.0	49	56	1.7
150	43.3	89	81	1.7
200	46.6	72	180	1.7
250	50.4	55	80	1.8
300	54.9	45	58	1.8
400	67.4	31	35	1.8
500	100.	21	22	1.7
550	141.			
600	0	12	13	1.6
800	— 4.	0		1.5
1000	—12.	—7		1.9

Similarly, the axial ratios at a standard temperature are taken as characteristic constants of structure (see XII), while their departures from the standard constitute characteristic thermal constants.

The dilatation may be stated quantitatively in a number of different ways. The most direct is the simple statement of the rate of change of specific volume with temperature: $\alpha' = \frac{dv}{dt}$. This may be called the *true dilatation.* It is the increase in volume, per degree, of a mass of one gram, and is a form of dilatation-constant much used in thermodynamic formulas.

For comparing the dilatation of different substances, having differing densities, it is more convenient to use the dilatation per unit volume rather than per unit mass. Since the volume varies with the temperature, there are two ways of stating this constant. The true dilatation at temperature t is either divided by the volume of a gram at temperature t, giving what might be called a *true coefficient of dilatation at temperature t:* $\alpha'' = \frac{1}{v} \cdot \frac{dv}{dt}$; or it is divided by the volume of a gram at some standard temperature, usually 0°C, giving what might be called a *true coefficient of dilatation at t referred to* 0°: $\alpha = \frac{1}{v_0} \cdot \frac{dv}{dt}$. The latter is the more commonly used, and is the constant usually referred to by the abbreviated term, *coefficient of dilatation.*

TABLE XX.3.

MEAN COEFFICIENTS OF THERMAL DILATATION (VOLUMETRIC) FROM 0°C, FOR THE MODIFICATIONS OF SILICA.

t °C	Values of $10^6\alpha_m$			
	Quartz	Tridymite	Cristobalite	Vitreous
—250	21.3			—1.05
—200	24.6			—0.6
—150	27.35			—0.1
—100	29.7			0.4
— 50	31.73			0.75
0	33.58	73	17	1.15
50	35.29	69	21	1.3
100	36.91	62	31	1.45
117		{60 {77		
150	38.50	81	44	1.55
163		{81 {94		
200	40.07	92	62	1.6
250	41.75	87	163	
300	43.55	81	147	1.67
350	45.6			
400	48.0	70	121	1.70
450	50.8			
500	54.5	62	103	1.70
550	61.3			
573	{66.1 {81.2			
600	77.6	54	89	1.68
700	65.8			
800	57.2	42		1.62
900	49.4			
1000	43.4	33		1.62
1100	38.3			
1200	34.1			

For convenience of calculation the dilatation is often stated in still another form, namely, as the *mean coefficient of dilatation from* 0°. This is the average dilatation per degree for the whole range of temperature from 0°

to t: $\alpha_m = \frac{1}{v_0} \cdot \frac{v - v_0}{t}$. If the true coefficient of dilatation varies with temperature according to the second-degree formula: $\alpha = a + 2bt + 3ct^2$, then the mean coefficient is: $\alpha_m = a + bt + ct^2$, and the actual volume is: $v = v_0 (1 + at + bt^2 + ct^3)$.

Occasionally, for the sake of precision in the statement of experimental results, some other temperature than 0°, say 20°C, or t', is taken as the standard, and t must then be replaced with $(t - t')$ in the above formulas.

Thermal dilatation of silica

Among the various forms of silica, quartz and vitreous silica have been the most carefully studied with respect to their thermal dilatation, while the volume changes of tridymite and cristobalite are not so well known.

Table XX.1 contains the most probable values for the density and kilovolume of the better-known modifications of silica over a wide range of temperature, but at a uniform pressure of 1 atmosphere. The data on which the table is based will be discussed in later sections. The relation of volume to temperature is shown graphically in Figure XX.1.

Table XX.2 contains the most probable values for the true coefficient of dilatation, α, over the same range of temperature as Table XX.1. The relation of α to temperature is shown graphically in Figure XX.2.

Table XX.3 and Figure XX.3 represent similarly the most probable values of α_m, the mean coefficient of dilatation from 0°.

Table XX.4.

Estimated Changes in Volume at the High-Low Inversions of the Forms of Silica.

	Inversion-temp., °C	Volume increase	
		cc per kg	Percentage of v_0
Low-quartz to high-quartz.....	573	3.25	0.86
Low-tridymite to lower high-tridymite	117	0.63	0.14
Lower high-tridymite to upper high-tridymite	163	1. (approx.)	0.2 (approx.)
Low-cristobalite to high-cristobalite	200 to 275	12.	2.8

Table XX.4 contains estimated values of the change in volume at the high-low inversions. This volume-change is almost impossible to determine with exactness, because it is difficult to tell where the rapid but continuous dilatation ends and the sudden or discontinuous change begins. , The best that can be done is to extrapolate the volume curve from lower temperatures upward and from higher temperatures downward to the inversion-temperature, and take the difference. The more accurately the dilatation curve is known in the neighborhood of the inversion, the more accurately can the sudden change be estimated.

Types of temperature-volume curves in silica

Quartz has a temperature-volume curve of type IIa (see Figure VII.1). The volume increases at a rapidly increasing rate as the temperature

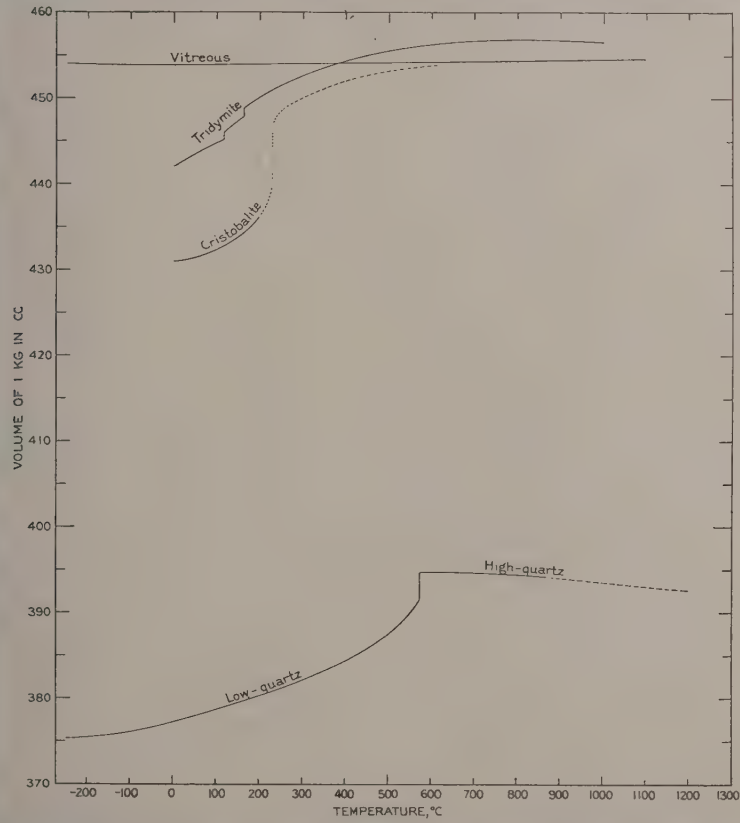


Fig. XX.1.—Temperature-volume curves for the principal forms of silica. The relative positions of the curves for tridymite, cristobalite, and vitreous silica are not known with exactness.

approaches 573° from below. In coming down from above 573°, on the contrary, no preliminary effect is detectable.

The volume-changes at the inversion-points of tridymite are very small and the data on dilatation are not as precise as those on quartz, so that it is not yet possible to name the type to which the temperature-volume curves of tridymite belong.

In contrast to quartz, cristobalite, in the mass, has a temperature-volume curve which is either of the general type III, or of type IV. The volume increases at an increasing rate with rising temperature, and decreases at an increasing rate with falling temperature. As has already been shown, however, the curve for each crystal in the aggregate must be of

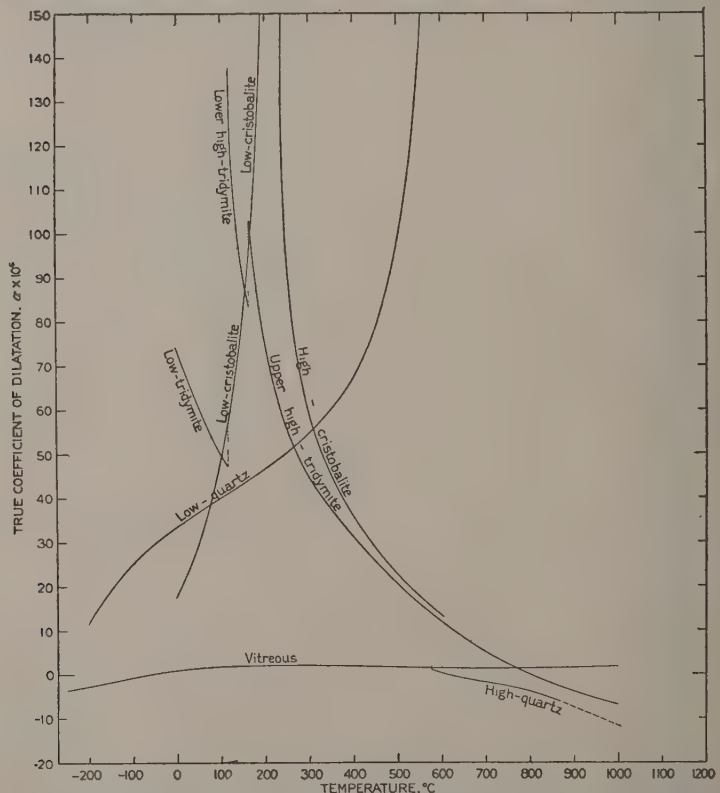


FIG. XX.2.—Relation of the true coefficients of dilatation to the temperature, for the forms of silica. The form of the curves for tridymite and cristobalite at the lower temperatures is very uncertain.

types III, II, or I, although the curve for the aggregate may be like IV.

Endell & Rieke [1] and Washburn & Navias [2] have observed dilatometrically that the volume curve of cristobalite is of the doubly rounded shape of type IV.

[1] Article cited in VI, note [41].

[2] Article cited in XIII, note [24].

Thermal deformation of quartz

The axial ratio of quartz decreases at an increasing rate up to the inversion-point at 573°C.

Since low-quartz and high-quartz are both hexagonal in the general sense, and have a principal axis which is not displaced at the inversion

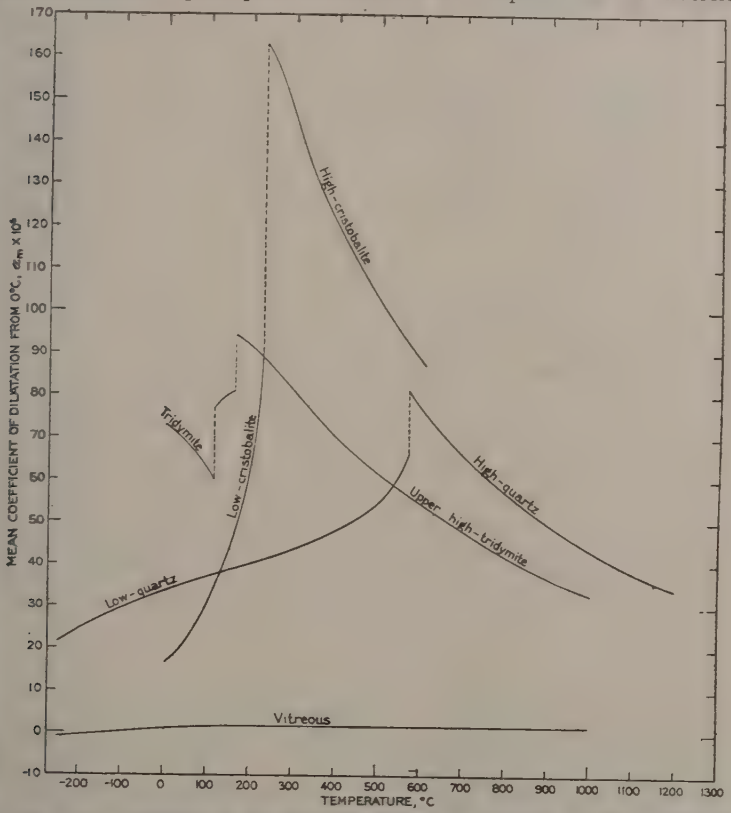


Fig. XX.3.—Relation of the mean coefficients of dilatation to the temperature, for the forms of silica. The form of the curves for tridymite and cristobalite at the lower temperatures is very uncertain.

point, the axial ratio may be considered as a constant which is common to both modifications. When so treated, it may be regarded as changing suddenly to a lower value at 573° after which it remains practically constant (or possibly decreases a little) up to 1250°C, beyond which no measurements have been made.

Table XX.5 contains the most probable values of the axial ratio of quartz over a wide range of temperature, all at atmospheric pressure. The data are shown graphically in Figure XX.4.

Table XX.5.

Axial Ratio of Quartz at Various Temperatures.

t °C	c	t °C	c
—250	1.1015	500	1.0956
—200	1.1014	550	1.0946
—100	1.1009	573	{1.0940 / 1.0922
0	1.1003	600	1.0921
100	1.0996	800	1.0916
200	1.0988	1000	1.0915
300	1.0979	1200	1.0916
400	1.0969		

Thermal deformation of other forms

The changes of axial ratio with temperature of low-cristobalite and the three modifications of tridymite have not been measured.

High-cristobalite is isometric in symmetry, and therefore undergoes no change in shape even should it have a measurable thermal dilatation.

Vitreous silica, if truly isotropic, should undergo a change of volume but not of shape. There is definite evidence, however, that many, if not all, pieces of vitreous silica are *œolotropic,* although the departure from isotropy is very slight. To a very small degree they differ slightly in properties in different directions, and hence should change shape slightly on heating or cooling. The character of the change will depend on the character of the æolotropy and the amount of the difference in thermal expansion with direction. This matter is more fully presented at p. 407.

Delayed dilatation

In the foregoing discussion of thermal dilatation it has been assumed that the effect follows promptly upon the change of temperature,—in other words, that there is no time-lag of dilatation. This is not always true. Upon the main dilatation on heating there may be superposed a small after-effect requiring a measurable time to complete, even though the temperature is constant; conversely, after the specimen has been cooled again to atmospheric temperatures, the initial volume is not attained immediately but is approached by a slow creep.

Delayed dilatation has long been known in metals, although it requires precise measurements for its detection. It is known to occur in vitreous silica, the effect being very minute because the dilatation itself is unusually small while the delayed dilatation probably amounts to no more than ½ per cent thereof. It is hence too minute to be measured directly, and has only

been detected in differential measurements where the effects were unequal in two specimens.

Delayed dilatation after heating and subsequent cooling has been observed in quartz, to the amount of 1.5 per cent of the dilatation, the effect disappearing after a few days.

It has not been looked for in tridymite and cristobalite.

Secondary constants. Mean linear thermal expansion

Since linear measurements are usually easier and more precise than volumetric, it is often convenient to express both the dilatation and the

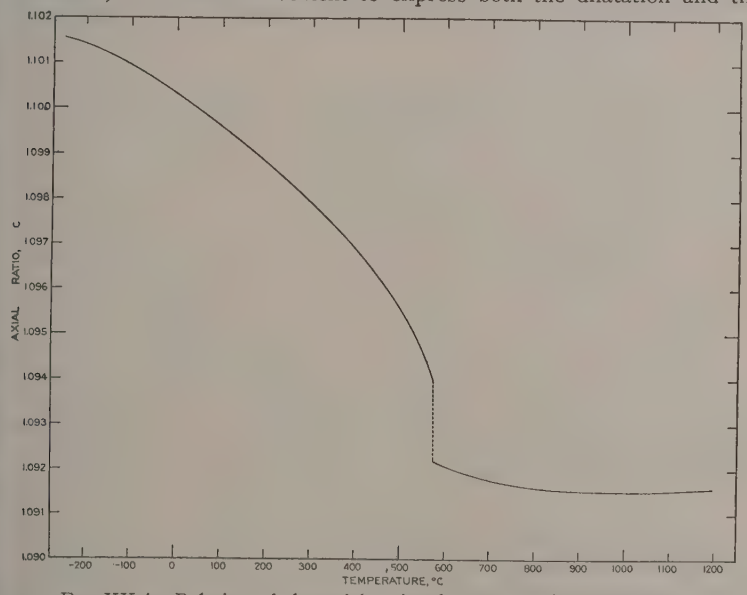


Fig. XX.4.—Relation of the axial ratio of quartz to the temperature.

change of shape in the form of the so-called "coefficients of linear thermal expansion".

Various linear measurements will be made use of as part of the available data for determining the best values for the thermal dilatation. The process may for the moment be considered to be reversed, and the best values for linear expansion may be deduced from the best values of dilatation. In this way the available volumetric and angular measurements are given a part in the linear expansions finally adopted.

Several different coefficients may be employed. They correspond exactly to the different kinds of coefficients of dilatation already mentioned. Those most commonly used are:

δ = the true coefficient of linear thermal expansion referred to 0°
δ_m = the mean coefficient of linear thermal expansion from 0°

For an isotropic substance they are defined by the formulas:

$$\alpha = 3\delta$$
$$\alpha_m = 3\delta_m + 3\delta^2_m t + \delta^3_m t^2$$
or $\alpha_m = 3\delta_m$ very nearly.

If the above definitions be extended to the case of an æolotropic substance such as quartz, the two coefficients are called, respectively, the *average true coefficient* and the *average mean coefficient* of linear thermal expansion. They are then purely fictitious quantities, which are realized approximately in the linear expansion of an aggregate in which the crystals are oriented in all directions. (See p. 387.)

Such values for δ or δ_m are readily calculated by dividing by 3 the values for α or α_m in Tables XX.2 and XX.3. The amount of the error in the assumption that $\alpha_m = 3\delta_m$ is stated at p. 387.

Table XX.6.

Axial and Equatorial Mean Coefficients of Linear Thermal Expansion for Quartz.

t °C	$10^6\delta_{m\parallel}$	$10^6\delta_{m\perp}$	t °C	$10^6\delta_{m\parallel}$	$10^6\delta_{m\perp}$
— 250	4.10	8.60	500	12.22	20.91
— 200	5.50	9.90	550	13.81	23.4
— 100	6.08	11.82	573	{15.00	25.15
0	7.10	13.24		{17.98	31.02
100	7.97	14.45	600	17.08	29.71
200	8.75	15.61	800	12.02	22.18
300	9.60	16.89	1000	8.83	16.97
400	10.65	18.50			

Linear expansions along axes

The thermal change of dimensions of an æolotropic crystalline substance, such as quartz, can be completely stated in another way than in terms of thermal dilatation and deformation, namely, by linear expansion coefficients in the directions of the crystallographic axes. Two such coefficients suffice for quartz: the linear coefficient parallel to the axis, which we may call the *axial* coefficient; and the linear coefficient perpendicular to the axis, the *equatorial* coefficient. They may be distinguished by attached or subscript symbols for "parallel" and "perpendicular."

Corresponding to the different kinds of coefficients already described we may then have: true axial and true equatorial coefficients, $\delta_\parallel$ and $\delta_\perp$; mean axial and mean equatorial coefficients, $\delta_{m\parallel}$ and $\delta_{m\perp}$. The following relations hold:

$$\alpha = \delta_\parallel + 2\delta_\perp$$
$$\alpha_m = \delta_{m\parallel} + 2\delta_{m\perp} + (\delta^2_{m\perp} + 2\delta_{m\parallel}\delta_{m\perp})t + \delta_{m\parallel}\delta^2_{m\perp} t^2$$
or $\alpha_m = \delta_{m\parallel} + 2\delta_{m\perp}$ (very nearly)

The error in α_m caused by neglecting the t term in the dilatation is a maximum at 573° where it amounts to —1.5 per cent of α_m. Values of the constants consistent with the dilatations and axial ratios already tabulated are given in Table XX.6.

The thermal deformations of tridymite and low-cristobalite are not known, and their crystallographic linear expansions consequently can not be given.

The experimental data on thermal expansion

Several methods are in use for measurement of thermal changes of dimensions. Some yield the deformation only, some the dilatation only, some yield both.

On a substance having only one axial ratio, such as quartz:

(A) The measurement of the change of a variable interfacial angle with temperature yields the thermal deformation only.

(B) The measurement of the linear thermal expansion within a crystal in two crystallographically different directions yields both the deformation and the dilatation.

(C) The measurement of linear expansion within a crystal in only one direction must be combined with (A) to yield dilatation or with (D) or (E) to yield deformation.

(D) The measurement of the linear expansion of an aggregate yields the thermal dilatation only.

(E) The measurement of the change of volume with temperature yields the thermal dilatation only.

Data of all these various kinds have been obtained for quartz, and their intercomparison becomes a matter of some complexity. Summarizing, it may be said that the tables and curves at the beginning of this chapter rest mainly on group (B) up to about 350°, above which temperature an extrapolation of the ratio $\delta_{m\perp} / \delta_{m\parallel}$ is combined with groups (A) and (C), while (D) and (E) serve as a check, especially above 573°.

Before proceeding with the comparisons it will be well to see what agreement may be expected between different specimens of quartz.

Constancy of the dilatation of quartz

The dilatation of a given specimen is reproducible within the limits of the most sensitive direct methods. Fizeau,[3] for example, used his specimen of quartz as a demonstration of the invariability of the dilatation of a crystalline substance. Measurements of the mean linear coefficient parallel to the axis, to 80°C, taken one year apart, gave values for $10^6\delta_m$ of 7.8118 and 7.8117. The agreement to 0.0001 is accidental or arithmetical, as the method could hardly have been sensitive to a difference of less than 0.005.

On the other hand, different specimens do not agree so perfectly.

[3] Fizeau, H., Compt. rend. Acad. Paris (1868) 66: 1005-1014.

Evidence of a real difference in the dilatation in different specimens of quartz was found by Buisson.[4] He examined the two cubes of quartz, one 4 cm and the other 5 cm on an edge, used by Macé de Lépinay & Buisson in their determinations of the relation between the cubic decimeter and the liter, and referred to below as C_4 and C_5, respectively (see p. 291). Both were perfectly transparent and without flaws. Measurements of the actual thicknesses were made by an optical interference method.

The dimensions of C_4 at various temperatures, when calculated back to 0° by Benoit's formulas for the two linear expansions, gave dimensions at 0° which agreed within the limit of error, and Benoit's expansion-formulas are therefore confirmed for this specimen. But similar measurements on C_5 did not thus agree, and a new pair of expansion formulas had to be derived, the rates of expansion for the range 0 to 40° being smaller than those of C_4, although they increased more rapidly with the temperature. The difference is of the order of magnitude of 1 per cent. The values of a and b in the formula

$$l = l_0 \ (1 + at + bt^2)$$

are compared below. (I have corrected the data to the international hydrogen scale, since the original temperatures are on the *verre dur* mercury-in-glass scale.)

	$10^6 a$	$10^6 b$
C_4 ∥ to axis	7.16	0.0080
C_5 ∥ to axis	6.99	0.0104
C_4 ⊥ to axis	13.25	0.0116
C_5 ⊥ to axis	12.91	0.0169

The difference in dilatation is confirmed by a difference in the temperature coefficient of refractive index, as shown by the following data, obtained at about 15°C:

	Values of $10^6 \frac{dn_\omega}{dt}$	
	Cd red	Cd green
C_4	—6.1	—5.9
C_5	—5.9	—5.7

As will appear later from Figure XX.11, the agreement between the data of Fizeau, Benoit, Scheel, Randall, and Nakamura is so close that if the measurements of Buisson stood alone we might reasonably suspect some unknown source of error in them. But Macé de Lépinay & Buisson[5] made about the same time a series on still another specimen of quartz (36-mm) which agreed with Fizeau and with Benoit, so that a real variability is strongly indicated.

The existence of such differences is further supported by the measurements of Scheel[6] (1907). He compared the expansion, between —190 and 16°, of the Reichsanstalt's standard quartz ring and another similar ring from the Zeiss works. The former expanded 0.42 per cent more than the Zeiss ring; the latter therefore deviates from the average in the direction of Buisson's abnormal specimen. Scheel's comparisons were made by the interferometer

[4] Buisson, H., *Sur les variations de quelques propriétés du quartz,* Compt. rend. Acad. Paris (1906) **142**: 881-883.

[5] Article cited in XXXI, note [3].

[6] Scheel, K., article cited in note [12].

method, with the large air correction eliminated by the use of a vacuum, and additional accuracy secured by the use of 9 different wave-lengths of light.

On the other side of the argument, however, stands the fact of delayed dilatation in quartz (see p. 392). If the final reading is taken too soon after cooling from a higher temperature, and if the mean of initial and final or the final alone is taken as the datum, then the coefficient will be too small. But it does not seem likely that this will account for the difference observed by Scheel, because he took the precaution of looking for delayed dilatation in his quartz, and found none.

It will be noticed that the downward extrapolation of Müller's data in Figure XX.11 agrees with Buisson rather than with the average. Reimerdes' result is lowest of all, but his data are more irregular than the others and the difference may be due to experimental error.

Unfortunately, in not a single instance is there a record of the geographical or geological source of the specimens of quartz used.

The experimental data on quartz

(*A*) *Measurement of angles*

The variation of certain interfacial angles of quartz with temperature has been determined up to temperatures above the inversion in two sets of measurements, one by Rinne & Kolb and one by Wright. Measurements at atmospheric temperatures have been made by Lang and by G. Müller, and at low temperatures by Goldschmidt.

If the effect which we have called "thermal deformation" were zero, the axial ratio would be unaffected by temperature, and the various angles would remain constant, so that the curves of Figure XX.5 would be horizontal straight lines. Instead, the angles are found to change with the temperature at an increasing rate, up to the inversion-point to high-quartz, where there is an additional and sudden change of axial ratio accompanying the change in symmetry.

The measurements on high-quartz indicate only a very slight further change with temperature. The measurements become less accurate as the temperature rises because of the large amount of light from the furnace itself, although this difficulty can be partly obviated by the use of an arc light and a blue filter.

Rinne & Kolb[7] measured 3 interfacial angles on a small crystal from Skole, Galicia, at 11 temperatures from 20° to 780°. The angles used were:

$(10\bar{1}1) : (\bar{1}101)$, between two faces of the primary positive rhombohedron,

$(10\bar{1}0) : (10\bar{1}1)$, between the hexagonal prism and primary positive rhombohedron,

$(10\bar{1}1) : (01\bar{1}1)$, between the primary positive and negative rhombohedrons.

Curves for these three angles are shown in Figure XX.5.

[7] Rinne, F., & Kolb, R., *Geometrisches zur Modifikationsänderung von α- in β-Quarz*, Centralbl. Min. **1911**: 65-74.

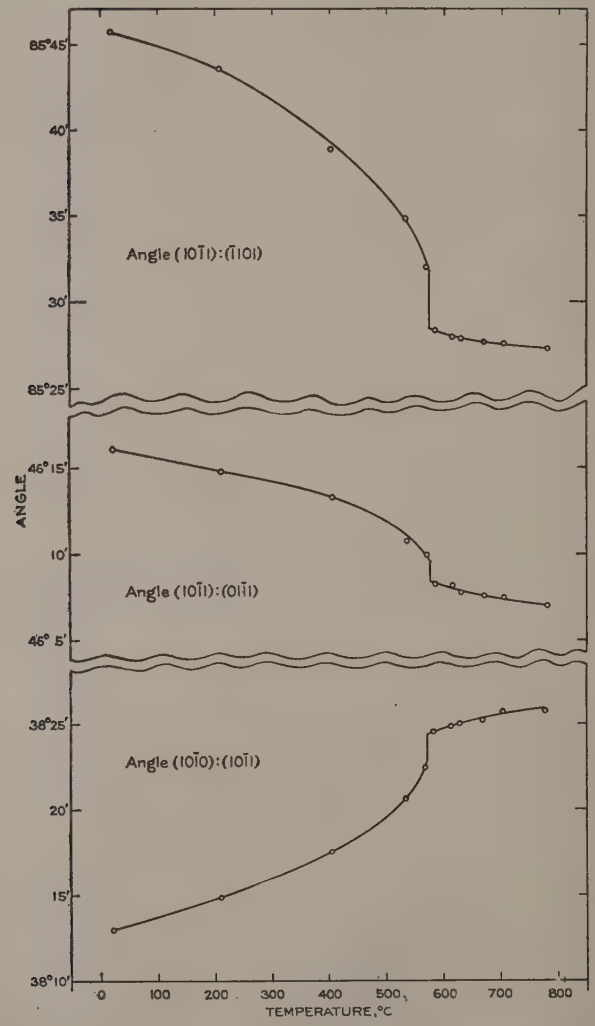


Fig. XX.5.—Thermal change of the interfacial angles of quartz. Rinne & Kolb, 1911.

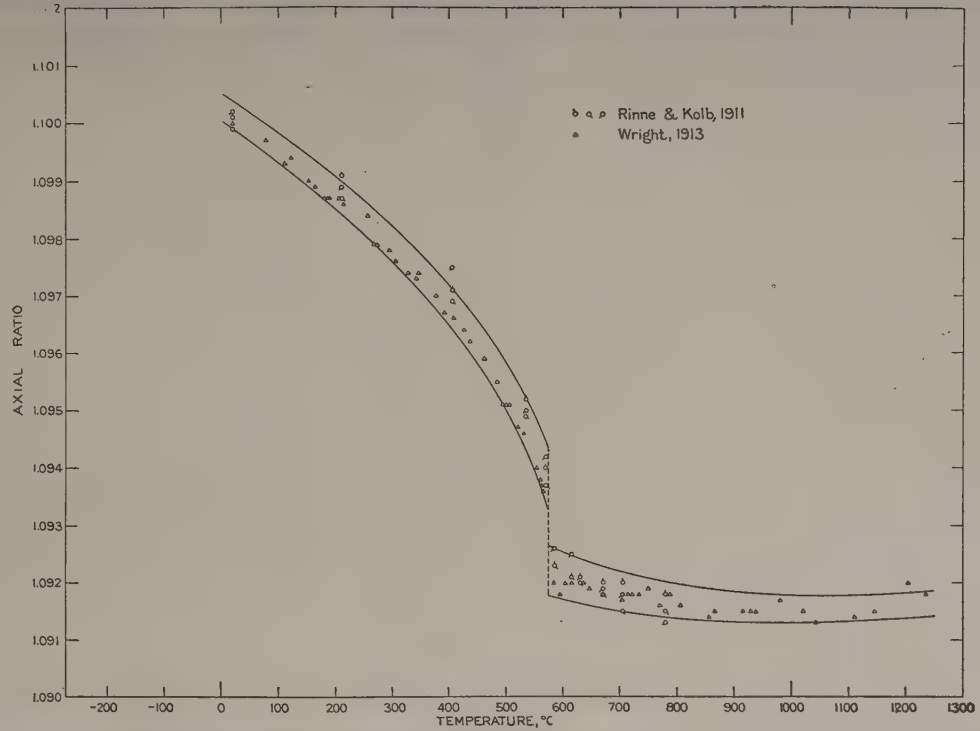


FIG. XX.6.—Experimental data on the thermal variation of the axial ratio of quartz, as determined by measurements of inter-facial angles. Rinne & Kolb (1911), Wright (1912).

The variation of the angular position of several faces on quartz crystals from Herkimer County, New York (U. S. National Museum no. 82925) was measured by Wright[8] at about 40 temperatures between 18° and 1239°C. The latitude and longitude of a group of faces was measured at each temperature on a two-circle goniometer having a furnace mounted at its center, and the group of results were then calculated in terms of the range of the polar angle ρ of a primary rhombohedron (the angle between the principal axis and the normal to a rhombohedral face).

Wright found that the variation of the polar angle of the primary positive rhombohedron of low-quartz could not be expressed empirically by any ordinary polynomial equation even up to the fifth degree. It could, however, be represented very accurately (within 0.1 circular minute, or less than the error of measurement) by an exponential equation of the form

$$y = ax + b(e^{ax} - 1)$$

If ρ = polar angle, t = temperature in °C, and T = temperature in °K, then the polar angle of the primary rhombohedron from 0°C to about 570°C is given by the formulas:

$$\rho = 51° \ 47.4' - [0.01132 \ t + 0.01335 \ (e^{0.01t} - 1)]'$$
$$\text{or } \rho = 51° \ 51.4' - [0.01132 \ T + 0.000871 \ e^{0.01T}]'$$

In order to compare the angular data with each other and also with the measurements of linear and volumetric expansion given in subsequent pages, I have calculated the values of the axial ratio c from the measurements of Rinne & Kolb and of Wright. The results are plotted in Figure XX.6. Practically all of the data fall between the two curves drawn in the Figure; the difference between the curves is hardly more than the experimental error, the scale of c being fairly large.

TABLE XX.7.

TEMPERATURE COEFFICIENT OF THE AXIAL RATIO OF QUARTZ AS DEDUCED FROM ANGULAR AND LINEAR MEASUREMENTS.

Observer	Angle and its coefficient	$10^6 \times$ temp. coeff. of c	
Lang	69° 53′ 43.553″ — 1.4066″t	— 6.84	
Müller	59° 59′ 21.82″ + 0.605″t	— 6.77	— 6.04
Müller	59° 58′ 30.23″ + 0.466″t	— 5.21	
Müller	60° 2′ 9.94″ — 1.099″t	— 6.15	
Average from Table XX.9		— 6.04	

Incidentally to their measurements on the refractive indices of quartz, both Lang[9] and Müller[10] determined the temperature coefficient of the axial ratio by means of angular measurements. Lang measured the thermal changes, over a range of about 5°, in the angle of a quartz prism whose prismatic edges were perpendicular to the principal axis. I have recalculated the results

[8] WRIGHT, F. E., article cited in VII, note [2].
[9] LANG, V. VON, Sitzungsb. Kais. Akad. Wiss. Wien (1869) **60**, II: 767-794.
[10] MÜLLER, G., article cited in XXXIV, note [4].

from Reaumur to C temperatures (correcting a mistake in the original published computation of the coefficient). Müller made measurements at 19 to 22 temperatures between —4 and 27° on each of 3 angles of an equilateral triangular prism, cut so that the principal axis was parallel to one edge of the base of the prism. The results of both sets are given in Table XX.7.

The temperature coefficient of the axial ratio is very nearly equal to the difference between the linear coefficients ($\delta_{\parallel} - \delta_{\perp}$), hence a comparison can be made with the data of Tables XX.5 and XX.9. The best value at 0° is -6.14×10^{-6}. This is in agreement with the curve of Figure XX.6 but is a more accurate value than could be deduced from that curve.

V. M. Goldschmidt [11] has measured the rate of change with temperature of certain angles of quartz at low temperatures, using small crystals from Finse, Norway. The changes are very small and therefore could not be measured very accurately. Measurements on angles $(10\bar{1}1)$: $(\bar{1}011)$ and $(10\bar{1}1)$: $(\bar{1}101)$ at about —60, —80, and —170° gave values for the change of angle per °C of —0.83 to —1.06 second, but the results are not very consistent. They serve to confirm the fact that there is no large or sudden change of shape in this range of temperature.

(*B*) *Linear measurements in two directions*

The most precise measurements of dilatation and deformation of quartz are those depending on linear measurements of the expansion of a piece of quartz crystal in directions parallel and perpendicular to the principal axis. The following observers have made measurements in the two directions, both on the same specimen: (1) Fizeau, 1866; (2) Benoit, 1888; (3) Le-Chatelier, 1889; (4) Macé de Lépinay & Buisson, 1904; (5) Buisson, 1906; (6) Lindemann, 1912; (7) Lindman, 1916; (8) Kozu & Saiki, 1924.

Nos. (1), (2), (4), and (5) are all within a very limited temperature range, namely, 0 to 80°C. The most exact of these are Nos. (2) and (5), while Fizeau's are less exact because of a less accurate temperature scale. Lindemann's measurements cover a much wider range (18 to —253°) but nevertheless seem nearly, if not quite, equal to the foregoing in precision; they furnish indispensable data for the very low temperature of liquid hydrogen. Le Chatelier's measurements, No. (3), cover a wide range of higher temperatures (15 to 1060°) but are not of high precision. Better data for the higher temperatures are provided by Nos. (7) and (8). (For further details see pp. 379 and 381.)

(*C*) *Linear measurements in a single direction only*

Uni-directional linear expansion measurements on quartz have been confined to the axial direction. Observations of this class have been made by: Pionchon (1889), Reimerdes (1896), Scheel (1902), Sahmen &

[11] Goldschmidt, V. M., *Über die Winkeländerung der Krystalle bei tiefen Temperaturen*, Zeitschr. Kryst. (1912) **51**: 1-27.

Tammann (1903), Eastman (1904), Sosman (1904), Auffenberg (1905), Randall (1905), Scheel (1907), Dorsey (1908), Bein (1912), Müller (1916), Nakamura (1918), and Pérard (1922).

The measurements of Sahmen & Tammann [12] were made with a differential mechanical dilatometer and extended to 1000°. All of the others were made by the interferometer method, which is more precise and accurate than devices using mechanical magnification.

The thirteen series belonging in the interferometer class constitute a fairly homogeneous set of data, all having been made carefully with attention to details and corrections and to the accuracy of the temperature measurement, and all are in very fair agreement. They include measurements from —190° through room temperature up to 540°.

Discussion of groups (B) and (C)

For the sake of completeness in the comparison it will be convenient to disregard the distinction between groups (*B*) and (*C*) and to consider all the linear measurements on crystals in one group, reclassifying them first according to method and second according to temperature-range.

The most precise methods are: (1) the interferometric method, and (2) the method of direct measurements on a bar. The interferometric uses a short specimen (1 to 10 mm) and measures its change of length in terms of the wave-length of monochromatic light, by taking advantage of the movement of the interference fringes produced between two reflecting surfaces. The bar method, for equal precision, must use a specimen 250 to 500 mm long, and so is better adapted to metals and glasses than to materials such as quartz.

Interferometer measurements

The interferometric method was devised by Fizeau. In his first measurements on quartz [13] he used a steel tripod and two 15-mm cubes side by side, with temperature intervals of approximately 7 to 36° and 7 to 63°. Later [14] the measurements were repeated with a tripod of platinum-iridium alloy, with readings between 12 and 80°.

Benoit [15] also used the Fizeau method. He made 38 observations in each of the two directions, on a cubical specimen 14 mm on an edge, over a range of temperature from 0 to 79°C. This is a very accurate set.

[12] Sahmen, R. v., & Tammann, G., Ann. Physik. u. Chem. (1903) **10**: 879-889.

[13] Fizeau, H., *Recherches sur la dilatation et la double refraction du cristal de roche échauffée,* Ann. Chim. et Physique (1864) (4) **2**: 143-185; Ann. Physik u. Chem. (Poggendorff), (1864) **123**: 515-526.

[14] Fizeau, H., *Mémoire sur la dilatation des corps solides par la chaleur,* Ann. Chim. et Physique (1866) (4) **8**: 335-361; Ann. Physik u. Chem. (Poggendorff) (1866) **128**: 564-589.

[15] Benoit, J. R., *Nouvelles études et mesures de dilatations par la methode de M. Fizeau,* Trav. et Mem. Bur. Internat. Poids et Mesures (1888) **6**, 193 pp. (Quartz, pp. 116-121 and p. 190).

The data of Macé de Lépinay & Buisson and of Buisson have been described (p. 372).

Lindman's [16] measurements were made with the Zeiss interferometric apparatus at Jena in 1899 on the same specimen as used earlier by Reimerdes (see note [24]). In the axial direction four series were made, at four or five temperatures each, covering the range 9 to 434°; in the equatorial direction, two series covering the range 10 to 334°. Temperatures were read with calibrated mercury thermometers. I have calculated the expansions from zero from his data, for use in Figure XX.10.

The thirteen sets of uni-directional interferometric measurements mentioned under (*C*) fall into two sub-groups: (*C 1*) measurements of the total expansion from room temperature, and (*C 2*) measurements of the expansion over short intervals at various temperatures, yielding the true coefficient of expansion at the mean temperature of each interval.

Subgroup (*C 1*).—Pionchon [17] measured only over the one interval 14 to 97°. Scheel [18] (1907) measured the interval 16 to —190°, and also (1902) [19] made 11 sets in 3 series going to 56 and 100°. Bein [20] made 13 measurements on 5 intervals between 16° and various higher temperatures up to 100°. Pérard [21] worked between 0 and 100° (details not given) using the 10-mm length standard of the International Bureau (see p. 830). Müller [22] obtained 14 values, each an average of several, up to a maximum temperature of 540°. Nakamura [23] made 2 measurements to about 50°.

Subgroup (*C 2*).—Reimerdes [24] obtained the true coefficient δ for 21 intervals, temperature range 6 to 234°. Auffenberg [25] used the same specimen, making 38 measurements on 9 intervals in the range 15 to 353°. Randall [26] used 52 intervals, 36 to 510°. Dorsey [27] used 5 40-degree intervals from —180 to 20°C. Eastman [28] and Sosman [29] used the same apparatus, taking measurements during cooling only; Eastman on 13 intervals, 85 to 235°, and Sosman on 9 intervals, 123 to 262°.

In the group as a whole Randall's set is the most complete; Scheel's and Müller's sets, the most accurate and precise. Most of Randall's temperatures,

[16] Lindman, K. F., *Om kvartsens termiska dilatation,* Acta Soc. Scient. Fennicae (1916) **46**: No. 5, 83 pp.

[17] Pionchon, Compt. rend. Acad. Paris (1889) **108**: 992-994.

[18] Scheel, K., Verh. Deut. Physik. Ges. (1907) **9**: 3-23.

[19] Scheel, K., Ann. Physik (1902) **9**: 837-853.

[20] Bein, W., Verh. Deut. Physik. Ges. (1912) **14**: 1097-1114.

[21] Pérard, A., J. de Physique (1922) (6) **3**: 257.

[22] Müller, A., Viertelj. Naturf. Ges. Zürich (1916) **61**: 107-119.

[23] Nakamura, S., Proc. Tokyo Math. Phys. Soc. (1918) (2) **9**: 342-345.

[24] Reimerdes, E., *Untersuchungen über die Ausdehnung des Quarzes durch die Wärme,* Inaug.-Dissert., Jena, 1896. 39 pp., 1 pl.

[25] Auffenberg, H., *Ueber die Abhängigkeit des thermischen Ausdehnungskoeffizienten von der Temperatur beim Quarz und einigen Gläsern mit anomal sich änderndem Elastizitätsmodul,* Inaug.-Dissert., Jena, 1905. 53 pp., 3 pls.

[26] Randall, H. M., Physical Rev. (1905) **20**: 10-37.

[27] Dorsey, H. G., Physical Rev. (1908) **27**: 1-10.

[28] Eastman, G. W., *The coefficients of expansion of quartz and of fused magnesia,* Thesis (unpublished) Mass. Inst. Technology, 1904.

[29] Sosman, R. B., Unpublished report, Res. Lab. Phys. Chem., Mass. Inst. Technology, June, 1904.

and all of Reimerdes', Auffenberg's, and Bein's, were measured with mercury-in-glass thermometers. This type is not very dependable above 100°; nor is it as exact at any temperature as the platinum resistance thermometer, used by Müller, by Scheel (1907), by Dorsey, by Eastman, and by Sosman, and also by Randall for a part of his series.

Measurements on bars

Lindemann[30] made direct measurements of the linear expansion of bars 100 mm long, at the temperatures of liquid oxygen, liquid air, and liquid

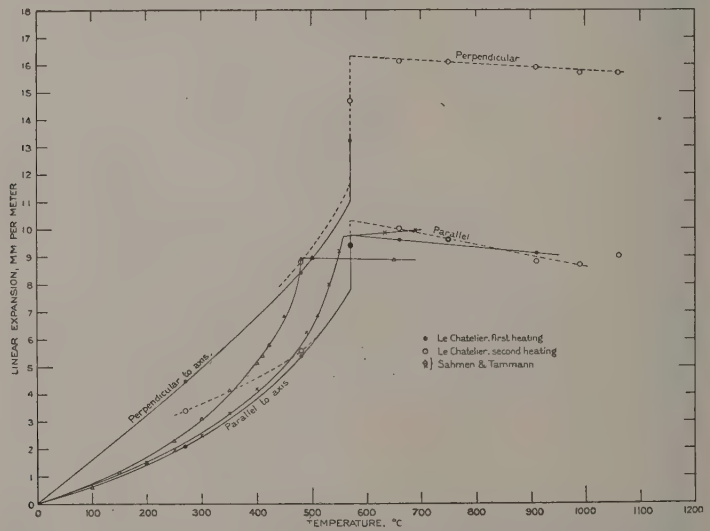


FIG. XX.7.—Experimental data on the actual linear expansion of quartz from 0°C, for the range 0 to 1100°. Sahmen & Tammann, Le Chatelier.

hydrogen. The bar was contained in a tube or frame of vitreous silica, while a rod of the same glass formed a continuation of the specimen bar up to the level of the measuring microscope. The quantity measured was therefore the difference in linear expansion between vitreous silica and the substance studied. As the precision was of the order of 2 to 5 per cent, the author considered the expansion of vitreous silica to be about equal to the possible error and therefore neglected it. Nevertheless, this constant is now known sufficiently well so that it seems to me justifiable, in recalculating the data into values of the mean coefficient for use in Figure XX.10, to make a correction for the expansion of vitreous silica. This has been done in the data presented in Table XX.8.

[30] LINDEMANN, C. L., *Ueber die Temperaturabhängigkeit des thermischen Ausdehnungskoeffizienten. II,* Physikal. Zeitschr. (1912) 13: 737-739.

TABLE XX.8.

LINEAR EXPANSION OF QUARTZ AT LOW TEMPERATURES. C. L. LINDEMANN.

Direction	Upper temp. °C	Lower temp. °C	Apparent Expansion of 100-mm bar μ	Total Corrected Expansion 0° to t		$10^6\delta_{m\parallel}$
				μ	t	
∥ to axis.....	15.9	—191.2	—109.5	— 95.0	—191.2	4.97
∥ to axis.....	—182.9	—193.1	— 4.0	— 91.8	—182.9	5.02
∥ to axis.....	—192.1	—252.7	— 12.0	—102.1	—252.7	4.04
⊥ to axis.....	17.7	—191.4	—219.0	—192.2	—191.4	10.04
⊥ to axis.....	—183.1	—193.1	— 8.0	—185.7	—183.1	10.14
⊥ to axis.....	—192.5	—252.7	— 27.4	—215.3	—252.7	8.52

Le Chatelier's measurements[31] were made photographically, the positions of the ends of a square bar $5 \times 5 \times 110$ mm being photographed through two telescopes at a fixed distance apart. Measurements were made at 3 temperatures below 573° and at 5 temperatures above 573°.

Kozu & Saiki[32] measured the linear expansion of 3 cylinders (dimensions not stated) parallel to the axis and 3 perpendicular thereto, in a differential apparatus of Chevenard's type in which the difference in expansion between a vitreous silica tube and the specimen was indicated by a mirror attached to a roller held between metallic extensions of the specimen and the silica tube. The temperature range was from 10 to 1200°C. The expansion was reversible in the first two specimens of each kind, which were heated only to 800°, but there was a permanent increase in length of about 0.2 per cent in the third specimen of each kind, which was heated to 1200°. This is not due to cracking,[32a] and may be the result of delayed dilatation (see p. 392). The critical limit varies between 950 and 1050°.[32a] The results for rising and falling temperature for the first two specimens, and for rising temperature only for the third specimen, are shown in Figure XX.8.

Curves

For convenience of comparison all the linear measurements on monocrystalline quartz, whether in one direction or two, are grouped in five diagrams.

Figure XX.7 contains the data by Le Chatelier and by Sahmen & Tammann, plotted as actual linear expansions from 0° to t.

Figure XX.8 contains the data of Kozu & Saiki, similarly plotted.

Figure XX.9 contains the data of Reimerdes, Auffenberg, Randall, Eastman, and Sosman on the true coefficient δ. Integration of the first three of these curves yields the total expansion from 0°, included in Figure

[31] LE CHATELIER, H., *Sur la dilatation du quartz*, Compt. rend. Acad. Paris (1889) **108**: 1046-1049; Bull. Soc. Franc. Min. (1890) **13**: 112-118.

[32] KOZU, S., & SAIKI, S., Sci. Rep. Tohoku Imp. Univ., Third Ser. (1925) **2**: 203-238; also in Jap. Journ. Astron. Geophys. (1924) **2**: 107-114.

[32a] Correspondence with Dr. Kozu, 1926.

XX.10. The last two have not been integrated for use in Figure XX.10 since they begin too far above 0°.

Figure XX.10 contains all linear data from —253° to 573°, plotted as actual linear expansions from 0° to t, in the same manner as in Figure XX.7.

Figure XX.11 shows on a larger scale the linear data between 0 and 100°, plotted in the form of values of δ_m, the mean linear coefficient from 0° to t. This is done because the data in this region are of high precision,

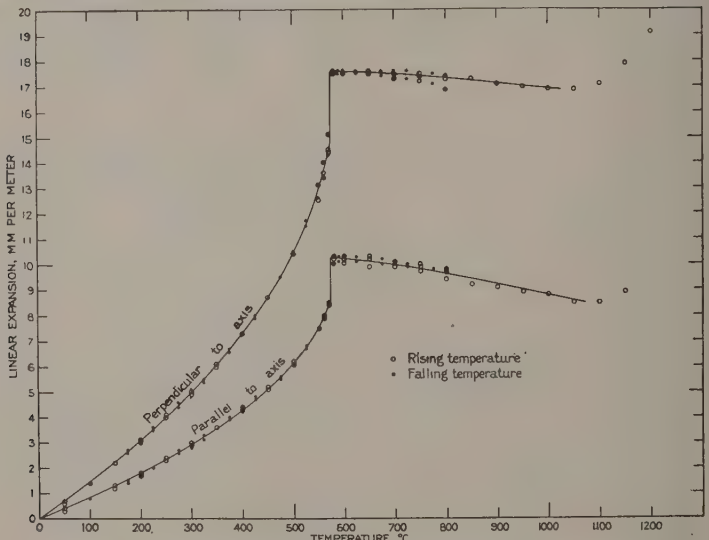


FIG. XX.8.—Experimental data on the mean coefficients of linear expansion of quartz from 0°, as measured by Kozu & Saiki.

and a plot of the actual linear expansions would not be on a sufficient scale to show the differences.

As is evident from Figure XX.7, one of the specimens used by Sahmen & Tammann appears to invert at 480°. The method is not, however, wholly reliable. The expansion is magnified mechanically, a method which always introduces uncertainty from variable contacts and back-lash of moving parts. The expansion is differential, and the accuracy depends, among other things, upon equality in temperature between a rod and two concentric tubes of porcelain, and also between the specimen and a surrounding silver tube. Although 90° seems a large error, I hesitate to believe that any specimen of quartz has an inversion point as low as 480° when numerous other determinations, using a variety of properties, all show that the inversion is always near 573°.

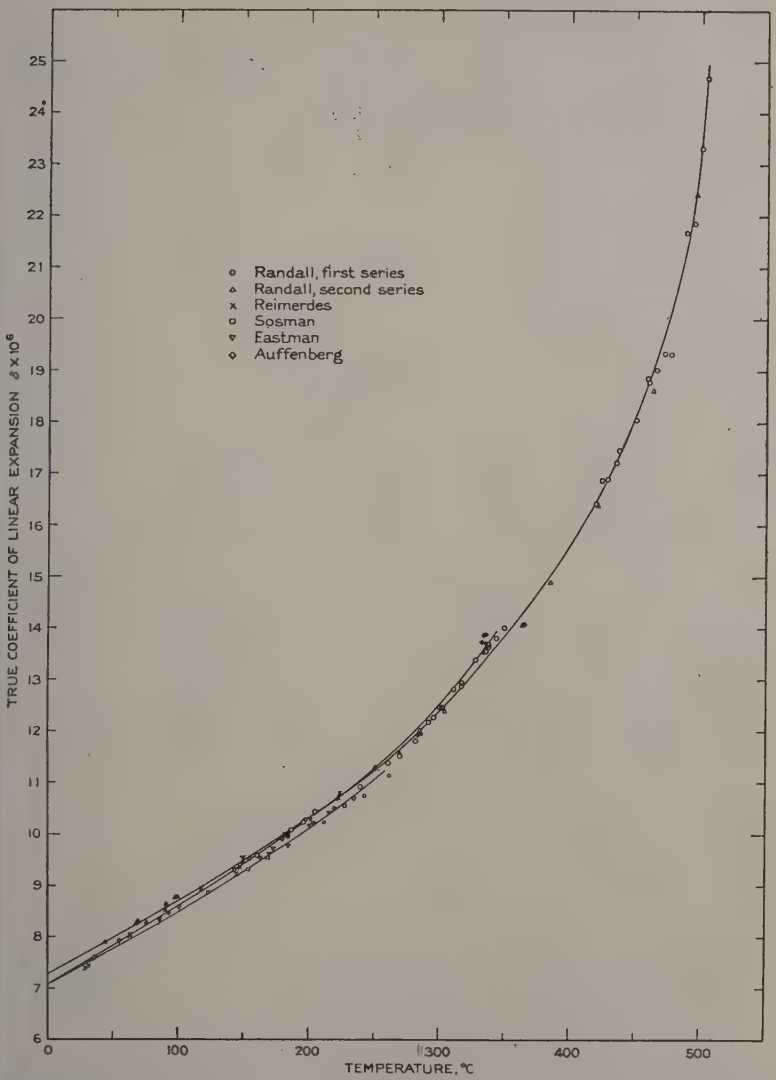


FIG. XX.9.—Experimental data on the true coefficient of linear expansion, δ, of quartz, parallel to the axis, at various temperatures.

Sahmen & Tammann's second specimen is in reasonable agreement with the value 573°.

A comparison of Le Chatelier's first and second experiment in each direction in quartz shows the effect of the cracking due to the inversion, in making the second expansion appear too large. (See p. 388.)

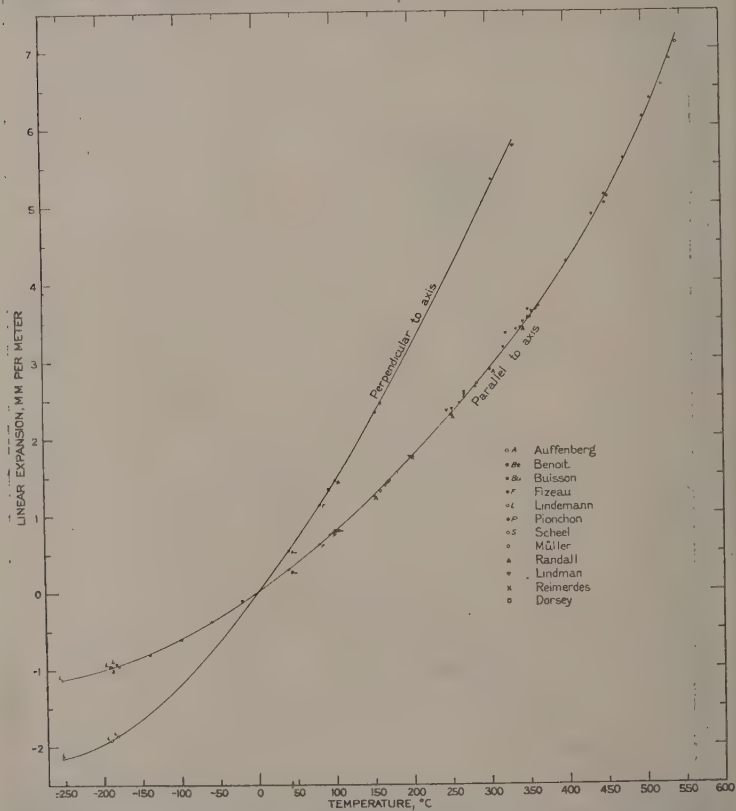


FIG. XX.10.—Comparison of experimental data on the actual linear expansion of quartz from 0°C, including values obtained by integration from Figure XX.9.

It is evident from Figure XX.9 that the results of Eastman and of Sosman are lower throughout their range than those of Randall, while the results of Reimerdes and of Auffenberg are lower than those of Randall only in the lower part of the range. The use of mercury thermometers by Reimerdes and by Auffenberg makes their temperature measurements distinctly less exact than the others. On the other hand, both Sosman and

Eastman used the method of spontaneous cooling, the apparatus being enclosed in a heavy insulated copper block which was heated to the maximum temperature and then allowed to cool slowly. It is assumed in this method that

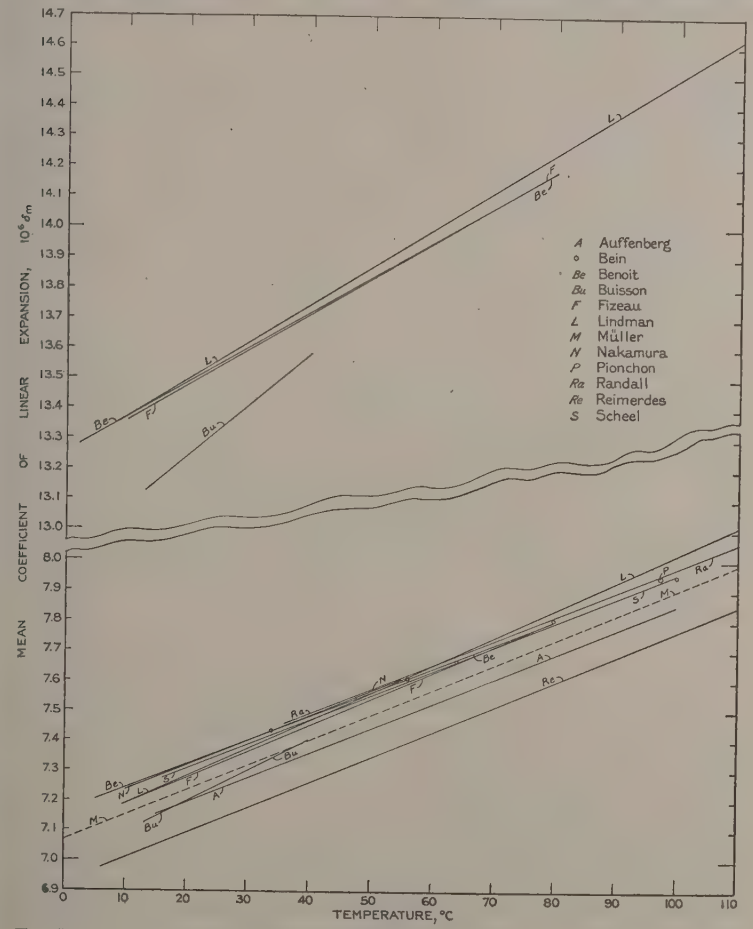


FIG. XX.11.—Comparison of experimental data on the mean coefficient of linear expansion of quartz from 0°C.

the difference in temperature between the resistance thermometer and the specimen of quartz is small and also constant. The method is a rapid one, but the results will perhaps not deserve full weight until the degree of exactness of these two assumptions shall have been proved experimentally.

Figure XX.10 contains total linear expansions from 0°. The measurements

between 0 and 100° are indicated in this Figure only by circular black spots at the upper limits of the different series. They differ so little that the curves are indistinguishable on this scale. They will be shown again on a larger scale in Figure XX.11.

Müller's and Lindman's expansion data, included in Figure XX.10, have been calculated from their original summarized tables. Values for the total expansion have also been derived from Randall's, Reimerdes' and Auffenberg's curves (Figure XX.9) by integration, and are plotted at even temperatures in Figure XX.10. Dorsey's data, being in a continuous series, are readily transformable into total expansions from 20° and can then be corrected to expansions from 0° by interpolation on his own curve.

The expansion thus calculated between —180 and 0° from Dorsey's curve is about 2 per cent greater than would correspond to Scheel's measurement at —190°, while the expansion between —20° and +20° is so much larger than would be interpolated from most of the other data as to throw doubt on the accuracy of Dorsey's method. His method of attaining a fixed temperature consisted in conducting heat through the steel vacuum-box, surrounding the specimen, into a quantity of liquid air below the box, by way of a projecting point on the bottom of the box. This necessarily calls for a temperature gradient in the walls of the box, and might also produce a gradient in the specimen.

The data between 0 and 100° are shown on a larger scale in Figure XX.11, and are expressed in the form of the mean coefficient δ_m instead of the actual expansion. The results are given in the form of the curves deduced and published by the authors themselves, the actual measured expansions being in several cases not on record. The temperature range actually covered by the data is indicated by the temperature limits between which each curve is drawn.

The most probable values for the coefficients, deduced mainly from the data compared in Figures XX.7 to XX.11, have already been presented at the beginning of the chapter.

Empirical relations between expansion and temperature

If the total linear expansion be expressed in the empirical formula: $l = l_0 (1 + at + bt^2)$, the mean linear coefficient from 0° to t (see p. 370) is: $\delta_m = a + bt$, while the true coefficient is: $\delta = a + 2bt$. Table XX.9 contains the values for a and b deduced by various observers from their experimental data.

A quadratic formula for the axial linear expansion (that is, a linear formula for the coefficient $\delta_{m\,ll}$) is fairly successful in expressing the data from 0° to about 300°, but it deviates a little at —190° and departs widely above 400°. The measurements of axial expansion at —190° may be included by adding another term, as shown by Scheel:

$$l_t[\text{from } -190 \text{ to } 100°] = l_0(1 + 7.085 \times 10^{-6}t + 9.386 \times 10^{-9}t^2 - 7.20 \times 10^{-12}t^3)$$

Lindman gives for the axial expansion:

$$l_t[\text{from } 9 \text{ to } 350°] = l_0(1 + 7.159 \times 10^{-6}t + 8.623 \times 10^{-9}t^2 + 1.87 \times 10^{-12}t^3)$$

$$l_t[\text{from } 9 \text{ to } 434°] = l_0(1 + 7.144 \times 10^{-6}t + 8.925 \times 10^{-9}t^2 + 0.146 \times 10^{-12}t^3 + 2.75 \times 10^{-15}t^4)$$

TABLE XX.9.

VALUES OF a AND b FOR QUARTZ IN THE FORMULA FOR MEAN COEFFICIENT OF LINEAR EXPANSION: $\delta_m = a + bt$.

	Parallel to axis		Perpendicular to axis		Range °C
	$10^6 a_{\parallel}$	$10^9 b_{\parallel}$	$10^6 a_{\perp}$	$10^9 b_{\perp}$	
Benoit	7.161	8.01	13.25	11.63	0 to 80
Buisson (C_s)	6.99	10.4	12.91	16.9	15 to 40
Fizeau	7.10	8.8	13.24	11.9	10 to 80
Lindman	7.099	9.25	13.25	12.6	10 to 300 (334 $\perp$)
Reimerdes	6.925	8.45			0 to 230
Auffenberg	7.03	8.25			15 to 100
Auffenberg	7.07	7.9			15 to 220
Scheel (1902)	7.144	8.15			16 to 100
Bein	7.153	8.08			16 to 100
Pérard	7.107	8.13			0 to 100
Randall	7.170	8.10			30 to 250
Müller	7.067	8.36			18 to 360
Nakamura	7.158	8.16			10 to 55

The results above about 300° cannot be satisfactorily combined with those below 300° in power series. The following formulas for axial expansion, of strictly limited range, have been suggested by Müller:

$$l_t[\text{from } 360 \text{ to } 450°] = l_0\{1 + [3628 + 13.00(t-360) + 0.01852(t-360)^2 + 0.000\ 067\ 21(t-360)^3]10^{-6}\}$$

$$l_t[\text{from } 500 \text{ to } 540°] = l_0\{1 + [5893 + 23.07(t-500) + 0.1031(t-500)^2]10^{-6}\}$$

the following by Randall:

$$10^6\delta[\text{from } 250 \text{ to } 470°] = 11250 + 16.5(t-250) + 0.0566(t-250)^2 + 0.000\ 134(t-250)^3$$

and the following by Auffenberg:

$$10^6\delta[\text{from } 220 \text{ to } 335°] = 10.50 + 0.0149(t-220) + 0.000\ 116(t-220)^2$$

(D) *Linear measurements on an aggregate*

An indirect method of determining the dilatation of quartz consists in the measurement of the thermal linear expansion of an aggregate. If the aggregate is composed of a large number of crystals oriented in all directions, then the dilatation is approximately 3 times the linear expansion. The more exact relation is

$$\Delta v = 3\Delta l + 3(\Delta l)^2 + (\Delta l)^3$$

where Δv is the dilatation of unit volume and Δl is the linear expansion of unit length. In the case of quartz, the maximum error caused by the neglect of the term $3(\Delta l)^2$ occurs at 573° and amounts to 1.8 per cent of the dilatation or 0.09 per cent of the actual volume at 0°. The term $(\Delta l)^3$ is quite negligible (0.01 per cent of the dilatation).

General considerations on the expansion of aggregates

Before presenting the data on the linear and volumetric expansion of aggregates it will be well to consider the different cases that may arise. This discussion will apply to the other forms of silica as well as to quartz.

Consider first a solid aggregate made up of grains of an isotropic substance, crystalline or amorphous. If heated so slowly that the temperature remains practically uniform, each grain will expand equally in all directions, and there will be no differential movement to separate the grains. On cooling, the aggregate will assume its original size and shape. (See Figure XX.12, A).

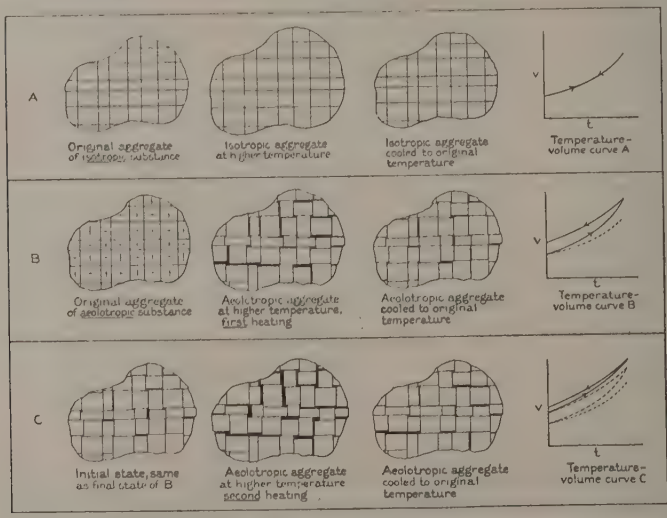


Fig. XX.12.—Diagrammatic cross-sections of a crystalline aggregate, to illustrate its thermal dilatation.

Now suppose the aggregate to be compact (non-porous) as before, but made up of grains of a hexagonal substance, such as quartz, which has a greater expansion perpendicular to the principal axis than parallel thereto. When the aggregate is heated the grains will push each other apart, as shown in Figure XX.12, B. The crossed lines in each grain in the figure represent the directions of greatest and least expansion.

This result can only be prevented if the grains are all oriented alike. If they are not oriented alike, open spaces will be produced throughout the piece. When the aggregate is cooled again these openings will tend to close, but the grains will never quite retrace their first movements, and some spaces will remain unfilled. There will be a permanent dilatation, or a permanent increase in length if one dimension only is being measured.

If the aggregate be now heated a second time, there will be a tendency to retrace the last cooling curve, but in addition there will be a small amount of new differential movement, resulting in an additional permanent dilatation which is not so large as the first (see Figure XX.12, C).

From Figure XX.12, B it is evident that the dilatation of the aggregate is greater than that of the substance.

The initial volume of Figure XX.12, C, however, is the final volume of Figure B. The relation of the curve C to the true curve for the substance can therefore not be deduced. The curve of C may run exactly parallel to the true curve, or it may run above or below it. The attainment of a reproducible dilatation curve by an aggregate whose entire previous history has not been recorded is therefore no proof that its curve represents the true dilatation of the substance itself.

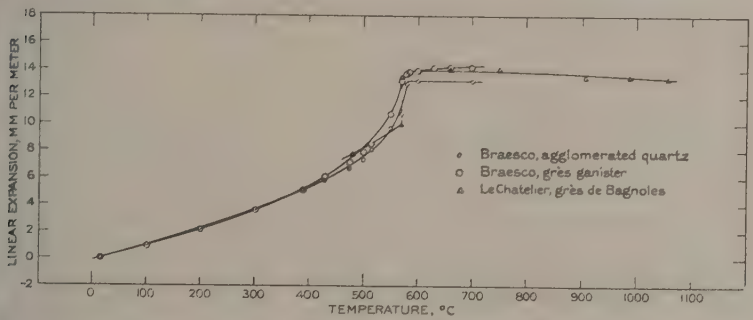


FIG. XX.13.—Experimental data on the actual linear expansion of a quartz aggregate.

Results with quartz aggregates

Linear measurements on aggregates have been made by Le Chatelier (1889) and by Braesco (1920).

Le Chatelier[33] measured the dilatation of all three of the principal crystalline forms of silica by measurements of the linear expansion of aggregates, but his temperature intervals were too large to show the true form of the expansion curves near the inversion points. He drew them all as if they were of type I (see Chap. VII) the scattered points permitting such a form as readily as forms II, III, or IV. Later measurements, not only of dilatation but of other properties also, show clearly that the quartz curve is not of type I, and that the curves of the other forms are also probably not of that type.

Braesco[34] determined the linear thermal expansion of several finely divided varieties of silica by agglomerating the material into a solid bar by means of water-glass. This seems at first sight to be a rather uncertain method. The expansion coefficient of such a compound bar might logically have any value between the expansion coefficient of the binder and that of the substance itself. In practice, the method worked out fairly well. Although the expansion

[33] Article cited.
[34] Article cited in IV, note [14].

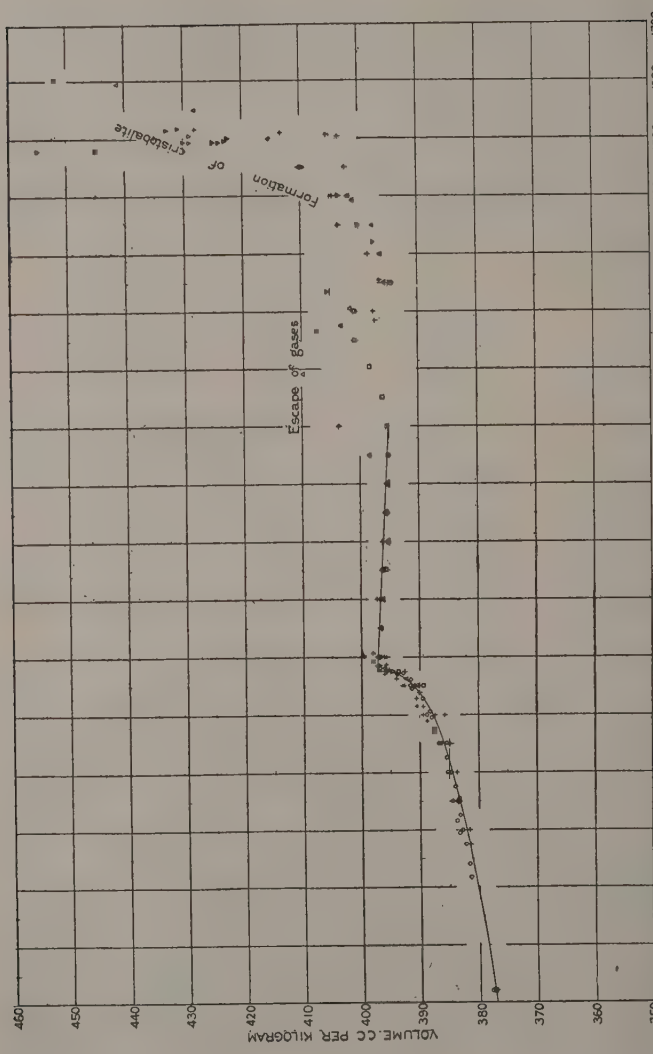


FIG. XX.14.—Experimental data on the actual specific volume of quartz at higher temperatures. Day, Sosman, & Hostetter, 1914.

coefficient of the binder was 20 times that of vitreous silica, the expansion of an agglomerated bar made of powdered vitreous silica with 5 per cent of its weight of water-glass was found to be the same as the expansion of a solid tube of vitreous silica, within the error of measurement (about a tenth of the expansion of the glass). The manner of making the bar evidently pressed the particles of glass into close contact, squeezing out the binder to one side so that it practically did not participate in the linear expansion of the bar.

In Figure XX.13 are plotted Le Chatelier's measurements on a bar cut from Bagnoles sandstone, and also Braesco's results on (a) a bar cut from "ganister" sandstone from Sheffield, England, and (b) a bar agglomerated out of powdered quartz with 5 per cent water-glass.

When compared with the most probable values derived from groups (A), (B), and (C), these experiments are found to give a dilatation which is too low, the value of $10^6\alpha_m$ for high-quartz at 573° derived from them being 70 to 75 as compared with 81 in Table XX.3. The curves as a whole are correspondingly low.

(*E*) *Volumetric measurements*

The principal set of volumetric measurements of the dilatation of quartz is that of Day, Sosman & Hostetter.[35] These measurements consist of 6 series, all on specimens of clear crystals from Minas Geraes, Brazil, and cover a temperature range from room temperature to 1600°C. The method used was a flotation method, with liquid tin or the lead-tin eutectic as immersion liquid. The underlying constant was the dilatation of pure artificial graphite, which was separately determined by linear measurements on a half-meter bar of the graphite, cut from a commercial electrode.

The experimental data on quartz are plotted in Figure XX.14. The circles, squares, etc., represent different series of measurements.

Since the volume is measured directly and not differentially, this is not as precise a method for the coefficient of dilatation as that depending on linear measurements. The principal uncertainty arises from the adhesion of bubbles of gas given off by the quartz, and the tendency is therefore toward high values. Calculation from the data represented in Figure XX.14 shows, in fact, that $10^6\alpha_m$ for high-quartz at 573° is 92 as compared with 81 in Table XX.3. The volume at 573° is 0.6 per cent high, while that derived from linear measurements on aggregates is 0.5 per cent low.

In general, the agreement of all the methods is fairly close.

Thoulet[36] devised a method for determining the dilatation near room temperature of a substance in small fragments, which consisted in causing the fragments to float in suspension in a solution of potassium and mercury iodides at two temperatures. Tested on quartz, the method gave the value $\alpha = 35.7 \times 10^{-6}$ between 19 and 45.6°. This agrees well with Table XX.3.

[35] Day, A. L.; Sosman, R. B.; & Hostetter, J. C., *The determination of mineral and rock densities at high temperatures,* Amer. Journ. Sci. (1914) **37**: 1-39; Neues Jahrb. Min. etc. (1915), Beil.-Bd. **40**: 119-162.

[36] Thoulet, J., Compt. rend. Acad. Paris (1884) **98**: 620-622.

Delayed dilatation

In most of the investigations on quartz quoted on pp. 373-391, no lag or delayed dilatation was observed. Scheel[37] looked for evidence of lag between —190° and room temperature but could find none.

Lindman[38] is the only investigator who has published any determinations of the lag at room temperature after quartz has been heated. After heating to 350°, he found an increase in length, parallel to the axis, amounting to 1.5 per cent of the total linear expansion. A similar but slightly greater increase was found in the equatorial direction. On standing at room temperature for several days the specimen gradually regained its initial dimensions.

Peters[39] has observed a lag of about one per cent of the expansion, in quartz heated to only 55°.

We have observed similar effects in platinum alloys[40] heated to 900–1400°, and they are known to occur also after cooling to low temperatures.

In view of the negative result obtained by Scheel, these observations invite to further study of the phenomenon. It remains quite possible that delayed dilatation in quartz can be proved and quantitatively studied at all temperatures. It must be taken into account in determinations of dilatation if the highest accuracy is to be attained.

The data on tridymite

The data on tridymite comprise linear measurements on agglomerated bars by Le Chatelier and by Braesco, and volumetric measurements by Washburn & Navias.

The linear data by Le Chatelier and by Braesco are plotted in Figure XX.15.

Le Chatelier's measurements,[41] made photographically on a bar 100 mm long, cut from a silica brick, indicate a maximum volume at about 700–800°, followed by a slight contraction. The existence of a true reversible contraction was assured by several repetitions. Further confirmation is needed, however, because Le Chatelier's specimen contained only 85 per cent tridymite, the rest consisting of about 9 per cent of silica combined with 3 per cent of CaO, 2 per cent of Fe_2O_3, and 1 per cent of Al_2O_3 (total impurities 6 per cent). The effect of these other substances upon the dilatation is unknown, but it is unlikely that they could cause a reversible contraction and it is therefore probable that Le Chatelier's curve is of the correct form at the higher temperatures, although it may not be quantitatively exact.

At the lower temperatures Le Chatelier's curve does not have enough points to bring out the existence of the two inversions subsequently found by Fenner. Braesco's curve, made on a bar cut from the same brick as was used by

[37] Scheel, K., article cited in note [25].
[38] Article cited in note [36].
[39] Personal communication.
[40] Day & Sosman, Carnegie Inst. Publ. (1911) No. 157: pp. 35, 63.
[41] Le Chatelier, H., *Sur la dilatation de la silice*, Compt. rend. Acad. Sci. Paris (1890) 111: 123-126.

Le Chatelier, shows two breaks, one at about 115°, the other at about 145°. The first agrees well with Fenner's temperature of 117°. The second is lower than Fenner's (163°).

As the higher temperatures are approached Braesco's curve flattens sooner than Le Chatelier's, but the form is not inconsistent with the existence of a maximum above 700°.

The value for the volume-change at the inversion points of tridymite and cristobalite in Table XX.4 depend almost entirely upon dilatometer measurements by Washburn & Navias.[42]

The dilatometer method for volume-change ought to be more dependable than the agglomerated-bar method used by Braesco (see p. 389). Washburn & Navias used a dilatometer of pyrex glass with a mixture of H_2SO_4 and

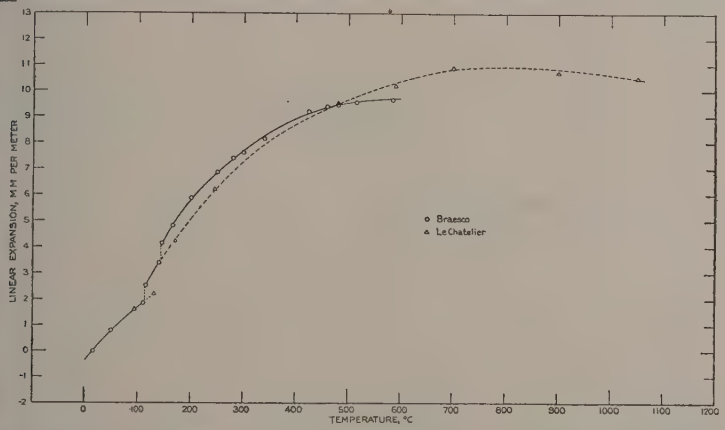


Fig. XX.15.—Experimental data on the actual linear expansion of a tridymite aggregate.

K_2SO_4, of density 1.94, as the expansion liquid. Using a 60-gram sample, they could make the dilatometric readings very sensitive.

Even with this sensitivity, they found it impossible to measure the small volume-changes at the inversion points of tridymite. The change at 117° was accordingly estimated by first determining the dilatation coefficient of the immersion liquid over a range of temperature, then determining the coefficients for tridymite above and below 117°, and finally determining accurately the difference between two dilatometer readings at 107 and 125° when the liquid and the tridymite were in complete equilibrium. This made it possible to calculate the volume change between these two temperatures more accurately than it could be read directly from a curve of dilatometer readings and temperature.

The value so obtained, 0.63 ± 0.06 cc per kilogram, agrees in order of magnitude with the less precise value of about 0.9 deducible from Braesco's curve.

[42] Article cited in XIII, note [24].

The volume change at the upper inversion was not measured by Washburn & Navias. It may be roughly estimated from Braesco's curve to be about 1 cc per kg.

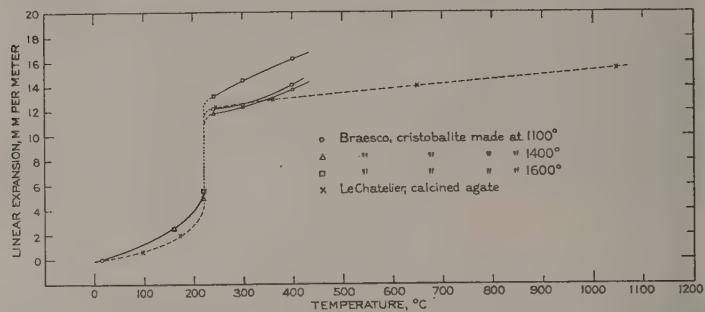

LINEAR EXPANSION, M M PER METER
TEMPERATURE, °C
o Braesco, cristobalite made at 1100°
△ " " " " 1400°
□ " " " " 1600°
x LeChatelier, calcined agate

FIG. XX.16.—Experimental data on the actual linear expansion of a cristobalite aggregate.

The dilatation-coefficients found by Washburn & Navias in the work just referred to are given below, compared with values estimated from the slope of Braesco's curve.

Temp. t	$10^6\alpha = \frac{1}{v_0} \cdot \frac{dv}{dt} \times 10^6$	
	W. & N.	Br.
About 105°	34 ± 27	48
About 180°	86 ± 18	89

These are not much more than orders of magnitude, considering the small changes of volume and length on which they depend, but they do indicate a higher true dilatation-coefficient for the high-modification than for the low-modification, a relation just the reverse of that in quartz. This relation in tridymite holds only for temperatures near the inversion range; at higher temperatures the coefficient appears to approach zero and become negative, like that of high-quartz.

THE DATA ON CRISTOBALITE

The experimental data on the dilatation of cristobalite are of much the same character as those on tridymite. They consist of measurements of the linear expansion of agglomerated bars by Le Chatelier and by Braesco, and dilatometer measurements by Washburn & Navias. These are supplemented by a number of qualitative observations by Rieke & Endell. X-ray measurements by Wyckoff at two temperatures supply information from still another point of view.

Le Chatelier's measurements [43] were made on 110-mm bars of agate and of silicified wood, which had been heated in a porcelain kiln at about 1500°, a treatment which converted the silica into cristobalite, although the fact of this conversion was at the time not fully recognized. The results are given in Table XX.10. It is not stated whether there was any prevailing direction of fibers in the specimens, as related to the axial direction of the bars.

A permanent increase of length was observed after the first heating in each case. Cracks formed in the specimen, and the density of the material was found to have decreased. After several repetitions this permanent expansion ceased to appear, and the thermal expansion then became reversible (but see p. 389). The last two columns contain the measurements made under this condition.

Braesco [44] prepared cristobalite by heating quartz, micro-amorphous silica, or vitreous silica in a gas furnace. The product was then agglomerated into a bar with a few per cent of silicate of soda.

Washburn & Navias' material [45] was made from chalcedony and flint at high temperatures, and was used in powder form in their apparatus, already described.

The data of Le Chatelier and Braesco are plotted in Figure XX.16.

TABLE XX.10.

THERMAL LINEAR EXPANSION OF BARS OF CALCINED CHALCEDONIC SILICA (LE CHATELIER).

Values are mm expansion per meter

t	Expansion on first heating			Reversible expansion after several heatings	
	Agate	Nodular chert (silex de la craie)	Silicified wood	Nodular chert	Silicified wood
15	0	0	0	0	0
270	...	0.40	0.48	...	0.48
480	0.89	0.86	0.93	0.95	0.90
570	1.64	1.20	1.18	1.30	1.27
660	2.52	2.00	...	1.40	1.31
910	4.32	2.50	1.86	1.40	1.32
990	...	2.40	1.93	1.40	1.34

Braesco's data are shown in Figure XX.16 in three sets, distinguished according to the temperature at which the cristobalite was prepared. That made at the highest temperature (1600°) gives the largest volume-change on inversion. Braesco ascribes the differences among the three to incomplete conversion at 1100 and 1400°. In view of what we have learned about the variation of the properties of cristobalite with its temperature of formation, it is also possible that these differences are real, and not due merely to different

[43] LE CHATELIER, H., article cited in note [41].
[44] Article cited in IV, note [34].
[45] Article cited.

percentages of cristobalite in the bars. The same is perhaps true of the considerable divergence between the curves of Braesco and Le Chatelier, the cristobalite being from two very different sources. The data leave much to be desired, however, and a more extensive systematic study is needed.

The measurements of Washburn & Navias do not give the whole volume change from room temperature, but do give the amount of change on inversion, which is by far the largest part of the dilatation to 300° and higher. Their results are:

Source of cristobalite	Volume change on inversion cc per kg
Chalcedony heated at 1430–1460°	13.1
Flint heated at 1430–1460°	15.0
Purified flint heated with Na_2WO_4 at 1500°	13.2
Mean	13.7

The corresponding value from Le Chatelier's curve is 11.9 cc, and from the average of Braesco's three curves, 11.0 cc.

Although no direct measurements have been made of the specific volume of cristobalite at higher temperatures, the following experiment[46] has been interpreted as indicating that it is not very different from the volume of vitreous silica at the same temperature. If a clear piece of vitreous silica is heated one to two hours at about 1500° and is then quickly removed from the furnace, the piece is seen to remain clear and transparent until no longer visibly red, when a few long cracks begin to form; then, between 200° and 300°, it suddenly begins to turn milky white, beginning from the outside. This occurs when the high-cristobalite inverts, with contraction of volume, into low-cristobalite.[47] The fact that at the higher temperatures the piece remains transparent and homogeneous, even though it probably consists of a mixture of glass and crystalline cristobalite, may be taken to indicate that the specific volumes of the two substances, at least below temperatures where the glass can flow, must be nearly equal, with just enough difference, however, to cause the formation of a few large cracks below 300° and before the inversion begins.

This deduction is in fairly good quantitative agreement with the data on dilatation already described. Starting with a kilogram-volume of 431 at 0°, the dilatation data would make the volume at 400° 448 at the least, and 452 at the greatest, as compared with 455 for the glass. The measured dilatation up to 400° thus covers 0.7 to 0.9 of the difference known to exist between cristobalite at room temperature and vitreous silica at 400°.

X-ray powder photographs (see XIII) give direct information as to the spacing of like planes of atoms, and if the symmetry and number of atoms in the unit cell are known, may be made to yield very precise data on volume

[46] Rieke & Endell, article cited in VI, note [41].

[47] The phenomenon seems to have been first observed by Bronn (*Der elektrische Ofen*, 1910: p. 285) who thought it was due to devitrification of a surface layer which had taken up impurities in the furnace and had become converted into an easily-crystallized silicate glass.

and dilatation. Wyckoff [48] made powder photographs at 290 and 430°C from cristobalite which had been crystallized from vitreous silica at 1560°, and found the dimensions the same within 0.1 per cent. This means a dilatation-coefficient from 290 to 430° which is nearly zero, like that of vitreous silica. The observation is not quite in accord with the general summary of most probable data in Tables XX.1 and XX.2, but it may well be that specimens of cristobalite differ in the character of their dilatation as they do in other ways. The most probable volume at 430° is in good agreement with the X-ray dimensions (see p. 209).

TABLE XX.11.

COEFFICIENTS OF DILATATION OF CRISTOBALITE. WASHBURN & NAVIAS.

Source	Temp. t	$10^3\alpha'$ $\alpha' = \frac{dv}{dt}$	$10^3\alpha$ $\alpha = \frac{1}{v_o} \cdot \frac{dv}{dt}$
From chalcedony, 1430–1460°	About 200	0.13 ± 0.03	0.27
Same	243	0.14 ± 0.02	0.28
From flint, 1430–1460°	About 200	0.09 ± 0.04	0.19
Same	243	0.14 ± 0.03	0.30
From purified flint with Na_2WO_4 at 1500°	202	0.11 ± 0.05	0.24
Same	About 247	0.15 ± 0.04	0.32

According to Callendar's measurements [49] on the linear expansion of vitreous silica, a rod, when so devitrified by heating at 1600–1700° that it is brittle, has nearly twice the expansion of the original glass, and the flattening or "change-point" at 1000° has disappeared. The increased expansion may reasonably be ascribed to the presence of cristobalite in the glass, but in amounts not enough to be easily visible.

Washburn & Navias [50] measured the coefficient of dilatation volumetrically, at temperatures above and below the inversion, with the results shown in Table XX.11.

The average value for α below the inversion is about 230×10^{-6}; above the inversion, about 300×10^{-6}. These are large dilatation-coefficients, much larger than those found for quartz and tridymite. From Braesco's curves it is seen that the dilatation is of the order of 60×10^{-6} at temperatures well above and below the inversion. It must be concluded that the values of Washburn & Navias are too near the inversion to be truly representative, and that they belong only to regions where the coefficient is changing rapidly with temperature, on the rounded shoulders of the S-shaped curve of volume.

From pyknometer measurements at 25 and 90°, Rieke & Endell [51] obtained the value $\alpha = 12 \times 10^{-6}$ for that range. Washburn & Navias, by similar measurements at 0 and 95°, obtained 10×10^{-6}, but doubt is thrown on the figure by an inconsistent result at 25°. Taken together with the compromise

[48] Article cited in XIII, note [5].
[49] CALLENDAR, H. L., article cited in note [56].
[50] p. 584 of article cited in XIII, note [24].
[51] Article cited in VI, note [41].

curve adopted for Figure XX.1 the results make it appear probable that the dilatation is small in the range 0 to 100°, increasing rapidly as the inversion is approached.

The results suggest the possibility that cristobalite, like vitreous silica, has a minimum volume at some lower temperature.

The data on vitreous silica

Most of our knowledge of the dilatation of vitreous silica comes from linear measurements in one direction only, on rods, tubes, or rings. The direct measurement of dilatation has not yielded as satisfactory results as the linear measurement because the quantity to be determined is relatively very small and volumetric measurements are usually not as precise as linear measurements.

Dilatation based on linear measurements

Linear measurements in a single direction have been made by the investigators mentioned below. The results of date 1903 and later are all of fair or high precision and are in good general agreement as to the amount and direction of the dilatation over a wide range of temperature. Certain variations are, however, undoubtedly present and will be considered in the sections following this general review.

For convenience of comparison the values of the mean coefficient of linear expansion, δ_m (see p. 370), are plotted in Figures XX.17 and 18. The precision of many of the measurements is such that a direct plot of expansion against temperature could not have been reproduced on a scale sufficient to show the differences. Figure XX.17 covers the entire range from —250° to 1100°C, while Figure XX.18 is a magnified portion covering only the range —250° to 200°C. Some of the measurements near room temperature and below, shown in Figure XX.18, are omitted from Figure XX.17.

Linear measurements on bars

Although the indifference of vitreous silica to sudden and large changes of temperature had been noted, no attempt was made to determine its actual coefficient of dilatation until 1890, when Le Chatelier [52] made a bar of calcined quartz agglomerated with 2 per cent of CaO, and heated it in a steelworks furnace. The thermal expansion of the specimen so obtained was found to be much lower than that of any of the crystalline forms of silica. Le Chatelier assumed that his bar was vitreous silica, but later results have indicated that it was in fact a mixture of vitreous with cristobalite and some

[52] Le Chatelier, H., article cited in note [43].

unchanged quartz; it is evident from the published data that the expansion of his bar was much larger than that of clear vitreous silica, and there was an irregularity near 570°.

A more reliable measurement was made in 1900, again by Le Chatelier.[53] Comparing the elongation of a prism of vitreous silica 10×50 mm with one of porcelain, he found an average linear coefficient to 1000° of 0.7×10^{-6}. The data indicate a maximum at about 750°, but the method is not very precise and later measurements show the coefficients to be too high.

At about the same time Barnett[54] (1898) measured the linear expansion of 3 fibers and a 1-mm rod of vitreous silica between room temperature and 100°, comparing them by means of micrometer microscopes with a comparator bar, and obtaining a coefficient of 0.3×10^{-6} for the fibers and 0.2×10^{-6} for the rod.

The next step in progress was to make length measurements of greater precision and make them on longer rods. This was done by Callendar in 1901 and by Holborn & Henning in 1903.

Callendar's measurements[55] were on a rod of vitreous silica about 1.5 mm in diameter and 400 mm long. It was heated by inclosure in a platinum tube about 3 mm in diameter which carried an electric current. The expansion of the platinum served as a measure of the temperature. Further details were published by Callendar[56] in 1912, together with additional measurements made with a similar apparatus. The expansion was found to be reversible and nearly uniform from 300 to 900°, with a mean coefficient δ_m of 0.58×10^{-6}.

After a flattening or change-point in the total expansion at about 1000°, the former rate was resumed, continuing to about 1400°, above which there was a contraction. The contraction above 1400°, like the expansion below 900°, was shown to be reversible. This last effect has not been studied by any later investigator, and can hardly be accepted without further confirmation by some other method, because of the possible error due to variable temperature gradients in Callendar's metal tube and silica rod.

Superposed upon the true positive and negative dilatations just referred to, there was observed a continuous permanent increase of length at 1400° and higher (see p. 476).

Concerning Callendar's measurements see, further, p. 407.

Holborn & Henning[57] made measurements at 250, 500, 750, and 1000° with micrometer microscopes, on a rod obtained from Heraeus, about 3×487 mm. I have recalculated their results using Chappuis' curve from 0° to room temperature. The results show the same tendency toward a maximum in the coefficient about 500 to 800° as is shown by most of the later high-temperature data, although Holborn & Henning themselves were content to put a lower estimate on their accuracy than it deserved, and reported that the coefficient had a constant value of 0.54×10^{-6}.

[53] Le Chatelier, H., *Sur la dilatation de la silice fondue,* Compt. rend. Acad. Paris (1900) **130**: 1703-1705.

[54] Barnett, S. J., article cited in XXIII, note [8].

[55] Callendar, H. L., *On the expansion of silica,* Chem. News (1901) **83**: 151-152.

[56] Callendar, H. L., Proc. Physical Soc. London (1912) **24**: 195-199.

[57] Holborn, L., & Henning, F., *Über die Ausdehnung des geschmolzenen Quarzes,* Ann. Physik (1903) **10**: 446-448.

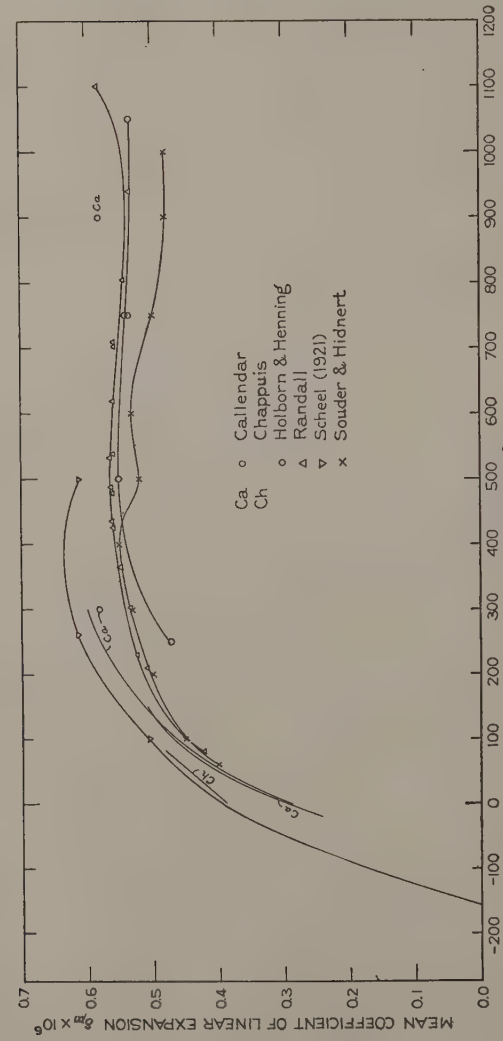


FIG. XX.17.—Experimental data on the mean coefficient of linear expansion, δ_m, of vitreous silica, from 0 to 1100° C.

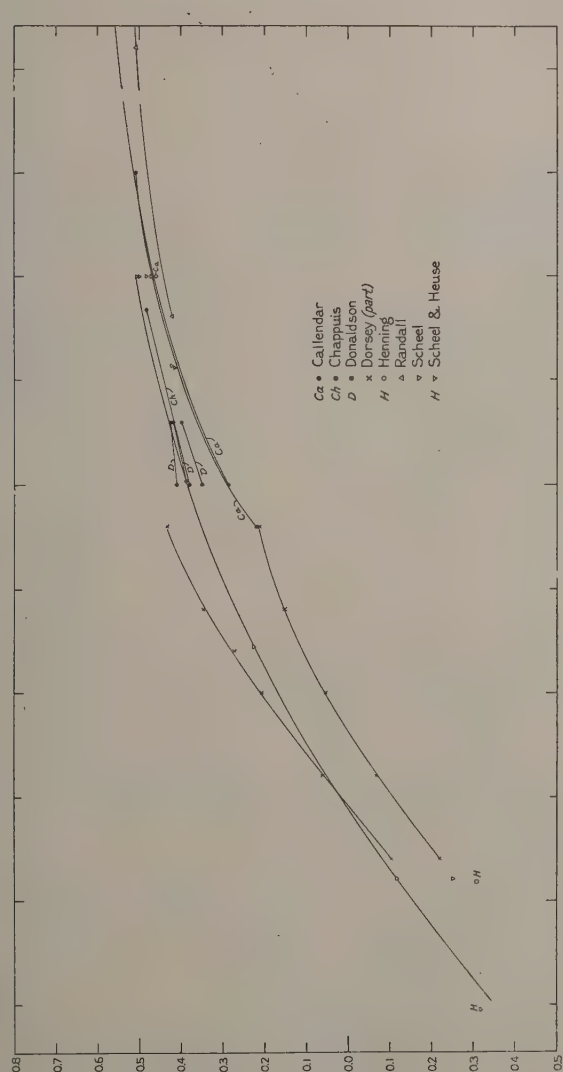


FIG. XX.18.—Experimental data on the mean coefficient of linear expansion, δ_m, of vitreous silica, from —250 to 200° C.

The recalculated results are:

t	$10^6\delta_m$
250	0.476
500	0.554
750	0.541
750	0.535
1000	0.534

At about the same time Henning made 6 comparisons at —191° (liquid air) between the expansion of 500-mm bars of vitreous silica and platinum. The absolute expansion could not be calculated until Scheel had measured the absolute expansion of platinum.[58] Henning's results were then calculated and published,[59] yielding -0.31×10^{-6} for δ_m at —191°.

Souder & Hidnert[60] have recently made measurements of length on 17 30-cm bars of vitreous silica, both transparent and opaque, using the method of measuring between suspended wires in contact with the ends of the uniformly heated bars. Three sets were made: one in pentane to —125°, one in oil to 300°, and one in air to 1000°. A minimum of length was observed at about —80°, although its temperature could not be placed with precision. Their mean linear coefficients at higher temperatures are:

t	$10^6\delta_m$	t	$10^6\delta_m$
60	0.40	500	0.52
100	0.44	600	0.53
200	0.49	750	0.50
300	0.52	900	0.48
400	0.54	1000	0.48

The irregularity between 400 and 600° (see Figure XX.17) is noteworthy. If present in Randall's curve it is of smaller magnitude and not sufficiently well marked to be brought out clearly by the data. The data of Holborn & Henning and of Scheel are not sufficiently numerous to show whether it is present or not. Further measurements of precision are needed at short intervals between 400 and 600°.

Donaldson[61] compared the silica meter standard of the National Physical Laboratory with their invar, nickel, and nickel-steel (43 per cent nickel) meters at temperatures of 0 to 30°C, and obtained the following linear coefficients:

Comparison with invar: $l = l_o\,(1 + 0.38 \times 10^{-6}t + 0.0013 \times 10^{-6}t^2)$
Comparison with nickel: $l = l_o\,(1 + 0.35 \times 10^{-6}t + 0.0016 \times 10^{-6}t^2)$
Comparison with nickel-steel: $l = l_o\,(1 + 0.41 \times 10^{-6}t + 0.0005 \times 10^{-6}t^2)$

Linear measurements on vitreous silica from 0° to 120° are said to have been made by A. Eagle[62] at the National Physical Laboratory before 1913,

[58] Scheel, K., article cited in note [18].
[59] Henning, F., Ann. Physik (1907) **22**: 631-639.
[60] Souder, W., & Hidnert, P., Sci. Paper Bur. Standards (1926) **21**: 1-23 (No. 524).
[61] Donaldson, H., *The coefficients of expansion of fused silica and mercury*, Proc. Physical Soc. London (1912) **24**: 186-194. Natl. Physical Lab. Coll. Res. (1913) **9**: 181-190.
[62] Harlow, F. J., article cited in note [55].

and to be in agreement with Harlow & Callendar's latest data (see p. 407). No details have been published.

Interferometer measurements

The best results, as a whole, on the linear expansion of vitreous silica have been obtained by the interferometer method of Fizeau (see p. 378). Chappuis (1903) was the first to apply it to vitreous silica. Similar measurements were subsequently made by Scheel, Minchin, Dorsey, and Randall, and have recently been continued by Peters & Merritt at the Bureau of Standards.

Chappuis [63] made 29 determinations on one specimen at temperatures between 2° and 84°, with the interferometer-dilatometer of the International Bureau of Weights and Measures. The general result is included in Table XX.12.

The first attempt to extend the use of the interferometer method to red temperatures or higher was made by Minchin [64] in 1907. He made 43 readings at temperatures from 200 to 950°. It was subsequently found that these determinations were affected by errors, and it was thought advisable to repeat the measurements, using the same specimen of vitreous silica and similar apparatus, but with improvements in both apparatus and method. This work was done by Randall [65] in 1910, the principal improvement in procedure being the production of the interference fringes in a vacuum, eliminating the large correction due to the changing refraction of air at higher temperatures, and removing the air films which are always troublesome in the interferometric method. A possible source of error exists, however, in the tilting of the interference system.

Randall made 35 readings at temperatures from 80 to 1100°, finding a definite variation of the coefficient with temperature. It rises to a maximum at about 500 to 600°, falls to a poorly-defined minimum in the neighborhood of 900°, and then rises again. I have recalculated the data, using Chappuis' curve for room temperatures, to obtain the mean coefficient from 0°. The results are plotted in Figure XX.17.

The measurements of Scheel and of Scheel & Heuse, all made by the interferometer method, furnish a very reliable set of data over a wide range of temperature (— 253 to 500°). Scheel's first series [66] included measurements at 56 and 100° on 2 cylindrical specimens made by Heraeus. In 1907 [67] he extended the measurements downward to — 190°, discovering the interesting fact that vitreous silica has a minimum volume, from which it expands both at lower and at higher temperatures. The existence of the minimum was confirmed by Scheel in a second investigation [68] in 1907, by measurements on a specimen of different origin and different shape, namely, a ring made by Zeiss. In 1914 Scheel & Heuse [69] showed that the expansion below the minimum continues to the temperature of boiling hydrogen, — 253°.

[63] Chappuis, P., article cited in XVIII, note [80].
[64] Minchin, H. D., Physical Rev. (1907) **24**: 1-21.
[65] Randall, H. M., Physical Rev. (1910) **30**: 216-235.
[66] Scheel, K., Verh. Deutsch. Physik. Ges. (1903) **5**: 119-123.
[67] Scheel, K., article cited in note [18].
[68] Scheel, K., Verh. Deutsch. Physik. Ges. (1907) **9**: 717-720.
[69] Scheel, K., & Heuse, W., Verh. Deutsch. Physik. Ges. (1914) **16**: 1-3.

Finally, Scheel[70] made measurements at 100, 260, and 500° to confirm the upward course of the curve. For comparison with other data I have calculated the values of δ_m, using Chappuis' curve from 0 to 16°C, and have plotted the results in Figures XX.17 and 18. The curve through Scheel's data in Figure XX.18 is his 3-constant empirical formula of 1907 (Table XX.12), and the curve in Figure XX.17 is his formula of 1921 joined on to the low-temperature curve.

In the same year (1907) in which Scheel announced the discovery of a minimum length in vitreous silica, Dorsey[71] discovered the same phenomenon in two specimens of vitreous silica whose expansion he measured at 20 or 40-degree intervals from 20° down to —180°. He used the interferometer method, in a vacuum. Both specimens attained a minimum length at about —80° and then expanded again at lower temperatures. The published results give only the expansion coefficient from interval to interval, but as the measurements form a continuous series it is easy to calculate from them the total expansion from 20°. This I have done, and have then made a correction, as before, for the expansion above 0°, estimating this correction from the original data on the true coefficients. The mean coefficient from 0°, δ_m, could then be calculated for comparison with the others in Figure XX.18.

Dorsey later made another series, of which only a brief abstract was published,[72] but he has very kindly furnished me with his original data, which are discussed at a later page. Only the highest and the lowest of Dorsey's curves are included in Figure XX.18.

Measurements by the interferometer method have been made recently at the Bureau of Standards by Peters & Merritt.[73] They show the slight flattening at about 800° already noted by several other observers, followed by an increase in the coefficient above 1000°. A maximum rate of expansion was found at about 1100° ($\delta = 1.2 \times 10^{-6}$).

Chappuis, Callendar, Donaldson, Scheel, and Scheel & Heuse have all stated their experimental results in the form of the familiar quadratic or cubic formula (see p. 386):

$$l_t = l_0 (1 + at + bt^2 + ct^3)$$

The values of a, b, and c published by these authors are assembled in Table XX.12. Because of the peculiar form of the dilatation curve of vitreous silica, these formulas are likely to give very erroneous results if used beyond the stated limits within which they were derived.

Direct (volumetric) measurement of dilatation

Threlfall[74] attempted to determine the dilatation of vitreous silica by measuring its volume directly, through the displacement of water at 22 to 74°C. Specimens weighing 2.7 to 14.2 grams were used. The results were not very satisfactory, 22 determinations giving values for α_m ranging from

[70] Scheel, K., Zeitschr. Physik (1921) **5**: 167-172.
[71] Dorsey, H. G., Physical Rev. (1907) **25**: 88-102.
[72] Dorsey, H. G., Physical Rev. (1910) **30**: 271-272.
[73] Merritt, G. E., Journ. Amer. Ceram. Soc. (1924) **7**: 803-808.
[74] Threlfall, R., article cited in XXIII, note [7].

TABLE XX.12.

VALUES FOR a, b, AND c FOR VITREOUS SILICA IN THE FORMULA $\delta_m = a + bt + ct^2$

		$10^6 a$	$10^9 b$	$10^{12} c$	Range, °C
Chappuis	1903	0.385	1.15	—	2 to 84
Donaldson	1912	0.38	1.1	—	0 to 30
Callendar	1913	0.29	2.5	—7.0	— 20 to 150
Scheel	1903	0.322	1.47	—	15 to 100
Scheel	1907	0.217	2.379	—	—190 to 100
Scheel	1907	0.388	1.682	—5.04	—190 to 100
Scheel & Heuse	1914	0.362	1.813	—3.40	—253 to 100
Scheel	1921	0.395	1.282	—1.70	0 to 500

$+37 \times 10^{-6}$ down to -22×10^{-6}. The change of volume is just about on the limit of sensitiveness of the method, and furthermore the dilatation of water is not known accurately enough to yield an exact value for the dilatation of silica by this method.

There is another method, not available for crystalline substances, for determining the dilatation of a glass; namely, to measure the liquid capacity of a bulb made of it. This determination can be made very accurate if the dilatation of the liquid is known accurately. Measurements of this kind, with mercury as the liquid, have been made by Harlow, by Eumorfopoulos, and by James.

I have recalculated Harlow's mean values, using the dilatation-coefficient curve of mercury recommended by Sears [75] as being best representative of the existing data. The results are contained in Table XX.13.

TABLE XX.13.

MEAN COEFFICIENT OF DILATATION FROM 0° OF VITREOUS SILICA, DERIVED FROM MEASUREMENTS OF THE APPARENT DILATATION OF MERCURY IN VITREOUS SILICA. $10^6 \alpha_m$.

EARLIER SERIES BY HARLOW (1911)

t °C	Prelim. bulb	85-cc cylindr. bulb	140-cc bulb containing silica tubes
100	1.45	1.43	1.46
184	—	1.52	1.54

LATER SERIES BY HARLOW (1913)

	70-cc spherical bulb	85-cc cylindr. bulb	140-cc bulb containing silica tubes
30			1.13
50			1.25
75			1.38
100	1.46	1.47	1.46
140		1.53	—
184		1.54	1.56
200		1.56	1.56
250		1.58	1.60
300		1.64	1.67

Eumorfopoulos [76] has not published details of his weight-thermometer measurements, but has given the curves for the dilatation of silica obtained

[75] SEARS, J. E., Proc. Physical Soc. London (1913) **26**: 95-96.

[76] EUMORFOPOULOS, N., *The expansion of mercury and of quartz*, Phil. Mag. (1912) **23**: 653-655.

by using three different dilatation formulas for mercury. From these it is possible to derive indirectly the values at 50 and 100° corresponding to Sears' curve. The results are:

	$10^6\alpha_m$
50°	1.39
100°	1.43

James [77] measured the apparent dilatation of mercury in a vitreous silica bulb of 100-cc capacity, at 100, — 20, — 30, and — 37°. He used values from Wheeler's summary [78] of the existing data on vitreous silica to calculate the dilatation of mercury. Taking Sears' curve for mercury, as before, we may reverse this calculation, obtaining thus the value 1.54×10^{-6} for α_m at 100°. The dilatation of mercury below 0° is not sufficiently well known to extend the calculation.

Part of the existing data on the dilatation of mercury have been obtained with metal and hard-glass bulbs, while part of the data on the dilatation of vitreous silica have been obtained by direct measurements of change of length. Measurements of the apparent dilatation of mercury in vitreous silica bulbs should logically, therefore, be treated as equations containing two unknown quantities, to be solved by combination first with the independent mercury data and second with the independent silica data, and then weighted according to the best estimate of the probability of each result. Although such calculations have not been formally carried out, Sears' curve is in effect the result of such a combination. The volumetric results just given have therefore not the same degree of independence as those represented in Figures XX.17 and 18, which contain the results of independent linear measurements.

The use of the most recent and most accurate mercury data in place of Sears' curve makes practically no difference at the lower temperatures, but reduces slightly the values at 200° and higher. The maximum reduction would be 0.15×10^{-6} in α_m at 300°.

As a whole, the volumetric results agree fairly well with the most probable set of values, as brought together in Table XX.3.

Variations of dilatation with direction in vitreous silica

In the absence of experimental evidence it had been assumed that vitreous silica is isotropic, at least with respect to thermal dilatation, until Harlow [79] published his measurements of the apparent dilatation of mercury in silica. The dilatation of silica to 100° deduced therefrom was considerably less than 3 times the then generally accepted value for the linear expansion. This led Harlow and Callendar to suggest that possibly the dilatation of a vitreous silica bulb is not uniform in different directions, and therefore can not be accurately calculated from the accepted linear expansion data.

Now this deduction depended upon a knowledge of the absolute dilatation of mercury, and Harlow had used Callendar & Moss's newly published data

[77] James, C. B., Trans. Roy. Soc. Canada (1914), Sect. III, **8**: 51-58.
[78] Wheeler, N. E., Trans. Roy. Soc. Canada (1914), Sect. III, **8**: 139-156.
[79] Harlow, F. J., Proc. Physical Soc. London (1911) **24**: 30-39.

on mercury,[80] which were in disagreement with the previously accepted data obtained by Chappuis.[81] Furthermore, in the following year Eumorfopoulos,[82] taking his own recent measurements of the apparent dilatation of mercury in a vitreous silica bulb, showed that if they were calculated with Callendar & Moss's data for mercury the dilatation of silica would come out zero at about 15°C, which seemed very unlikely. Other critics, also, pointed out that the double disagreement on mercury and silica called for more than the usual degree of confirmation.

This confirmation appeared at first to be forthcoming. In 1912 Callendar [83] published linear measurements made by the interferometer method on a tripod cut from a 2-cm vitreous silica tube, and a narrow ring standing on edge cut from the same tube. The temperature range was 18 to 90°. The measurements yielded an apparent difference between the parallel and perpendicular directions of the tube which was surprisingly large. The mean axial coefficient from 18 to 90° was found 0.20×10^{-6} greater than the mean radial coefficient, the value of the axial coefficient [84] being 0.46×10^{-6} from 0 to 100°.

Harlow and Callendar were not entirely satisfied with this result and made further measurements which were published in 1913. In these determinations Harlow [85] made a direct test of the supposed variability of dilatation of silica with direction by comparing the apparent dilatation of mercury as determined in cylindrical vitreous silica bulbs with that determined in a spherical bulb. The two kinds of bulb agreed within 1 in 18000, indicating that the aeolotropy could not be as large as Callendar at first supposed, and that the dilatation of these bulbs could be safely assumed to be 3 times the linear expansion (see Table XX.13 for the volumetric results).

In reporting on this set of experiments, Callendar [86] stated that specimens of vitreous silica which had been exposed to high temperatures gave lower results for expansion over the range 0 to 300° than specimens which had not been heated above 300°. Vitreous silica rods "showed at first some peculiarities due to intrinsic strain, but settled down into a cyclic state" in which their mean coefficient of linear expansion could be represented by the formula: $10^6\delta_m = 0.780 - \frac{86.50}{t + 175}$.

The axial (lengthwise) expansion of 4 vitreous silica tubes was also measured. This could be represented for the range —20 to 150° by the formula already indicated in Table XX.12, which agrees over this range with the formula found for the rods, but cannot be used for extrapolation to 300°.

The difference between the radial and axial expansion of tubes was also tested. "Differences of the order of 5 or 10 per cent in the expansion in different directions appeared to be persistent, and were not removed by heating

[80] Callendar, H. L., & Moss, H., Phil. Trans. Roy. Soc. (1911) A, **211**: 1-32.
[81] Chappuis, P., Trav. Mem. Bur. Int. Poids et Mesures (1907) **13**: 31 pp.
[82] Eumorfopoulos, N., article cited.
[83] Callendar, H. L., *Anisotropic expansion of a drawn tube of vitreous silica,* Phil. Mag. (1912) **23**: 998-1000.
[84] Callendar, H. L., Zeitschr. Instrumentenk. (1912) **32**: 194-195.
[85] Harlow, F. J., *The thermal expansions of mercury and fused silica,* Proc. Physical Soc. London (1913) **26**: 85-94.
[86] Callendar, H. L., Nature (1913) **92**: 467.

the specimens to 1000°C or cooling in liquid air. It was concluded that the differences in the radial coefficient might be due to distortion of the ring."

The absence of detailed data leaves this question of aeolotropy in the dilatation of vitreous silica undecided. We may say conservatively that it is more likely than not that there is a difference between the axial and radial dilatation of drawn silica rods and tubes, but that its magnitude has not been definitely determined.

Differences in dilatation between different specimens of vitreous silica

Scheel [87] found a difference which was slight, but apparently greater than experimental error, between the dilatations at 100° of two transparent cylindrical specimens, both made by Heraeus. This is shown by the following comparison:

	Expansion 15 to 100°	$10^6\delta_m$ at 100°
Cylinder 3.7 mm in diameter.....	42.2 μ per m	0.482
Cylinder 7 mm in diameter.....	41.2 μ per m	0.472

When measurements were extended by various investigators to liquid-air temperatures, larger differences began to appear. Dorsey [88] used two specimens: (1) a ring cut from a "clear but not transparent" piece of tubing, whose density (2.01) shows that it must have contained about one-tenth its volume of bubbles; (2) a perfectly transparent ring cut from a quartz-glass mercury arc lamp. The difference between the two was easily measurable.

Scheel [89] then compared the low-temperature expansion of one of his original Heraeus cylinders with that of a vitreous silica ring melted, cut and polished by Zeiss, finding a difference comparable with that observed by Dorsey. A third specimen was added by Scheel & Heuse.[90] The results are as follows:

	Linear expansion 16 to — 190° μ per meter	Temp. of minimum length	Expansion from 0° to minimum μ per m
Cylinder from Heraeus	41	— 46°	— 10
Ring from Zeiss	15	— 84°	— 18
Cylinder from Silica Syndicate *	32	— 68°	— 12

* Presumably. Called "Silicat Comp. London" by Scheel & Heuse.

Dorsey [91] then studied the effect of quenching and annealing upon the dilatation at low temperatures. Only a brief abstract of the results has been published, but Mr. Dorsey has very kindly sent me his original data from which I have calculated the data presented in Figure XX.19. The upper curves (A) of parts I and II of the Figure represent data published in 1907. The lower curve (B) of I is for a piece of the same glass (a translucent specimen) which has been heated to bright redness and quenched. The lower

[87] Scheel, K., article cited in note [68].
[88] Dorsey, H. G., article cited in note [71].
[89] Scheel, K., article cited in note [18].
[90] Scheel & Heuse, article cited in note [69].
[91] Dorsey, H. G., abstract cited in note [72].

curve (B) of II is for a piece of clear transparent vitreous silica cut from a mercury arc lamp and similarly quenched.

The curves of III are for a new specimen from the Silica Syndicate. Curve A is for the original glass; B, the same, annealed; C, the same, heated in a blast lamp flame and quenched in water. The dashed curve, inserted for comparison, represents Scheel's formula of 1907 (Table XX.12).

Pieces of rod and capillary tubing were also tested, which were in such a strained state that when scratched with a diamond they would crack all the way around. An attempt to determine the expansion of this material, by using three small pieces of equal length at the vertices of a triangle in place of the usual ring specimen, failed because the pieces expanded so unequally that the interference bands rotated or changed in width instead of progressing across the field.

It is evident from Figures XX.18 and XX.19 that the differences which accompany the change from the annealed to the rapidly quenched condition are of the same magnitude as those previously found by Dorsey and by Scheel between different specimens. The curve of the annealed is, on the average, about 0.06×10^{-6} above the curve of the quenched glass. This corresponds to a difference of about one-sixth at 0°.

Merritt[92] has observed a difference in dilatation between quenched and annealed specimens in the same sense as that just described, but apparently smaller in amount.

At higher temperatures, some interesting results have been obtained by Blackie[93] by a very sensitive differential method. He found that the transparent and the opaque varieties of vitreous silica differ measurably in dilatation between 0° and 800°. They differ in four ways:

(1) In absolute magnitude of the dilatation. The difference is at most about 8 per cent of the quantity itself, and is usually much less than that.

(2) In the shape of the temperature-expansion curve. The opaque glass has the greater expansion at the lower temperatures but falls back until the two kinds become equal in total expansion at about 450°. The transparent then expands the faster.

(3) In the shape of the return-curve or temperature-contraction curve. The opaque at first contracts the faster, but is soon overtaken by the transparent which then contracts the faster of the two down to atmospheric temperatures.

(4) In the amount of delayed dilatation after heating and cooling. If heated above 500° the transparent is the slower of the two to return to a constant length, but the reverse was the case in one experiment when the maximum was 360°. The difference persists for several days and is greater for temperatures above 500° than for those below 500°.

A typical curve of these effects is shown in Figure XX.20. All of these effects fall within a range of a few per cent of the dilatation,

[92] Merritt, G. E., pp. 805 and 808 of article cited in note [73].

[93] Blackie, A., *On the behaviour of fused silica at high temperatures,* Trans. Faraday Soc. (1911) 7: 158-165.

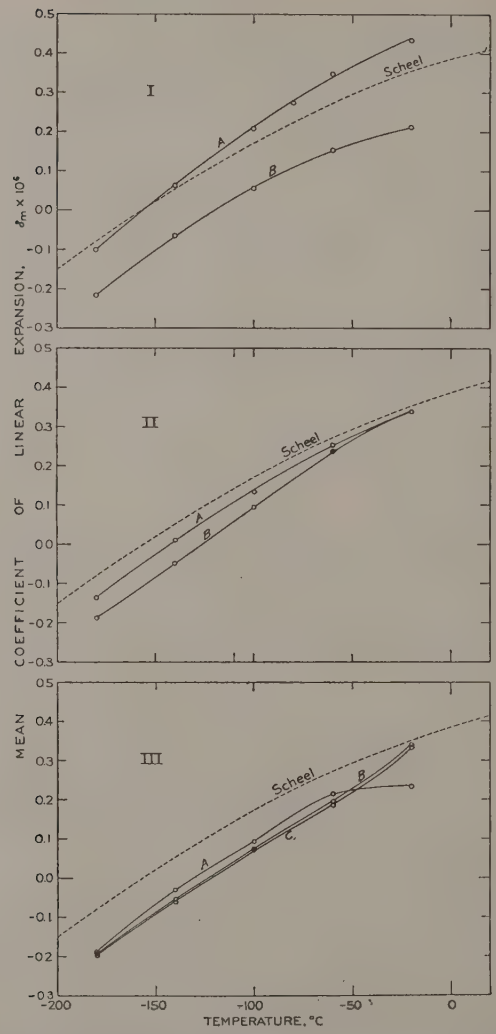


FIG. XX.19.—Effect of quenching and annealing on the mean coefficient of linear thermal expansion of vitreous silica below 0°C. Dorsey, 1907-1910.

which is itself a very small quantity. The differences are therefore extremely small and almost inaccessible to direct measurement. They have been measured by Blackie by comparing the change in length of an opaque and a transparent piece in the form of two concentric tubes. The two were sealed together at one end, while the free ends were supplied with parallel plane surfaces between which rolled a needle carrying a mirror. The difference of length was thus obtainable to 1 in 10,000,000.

Souder & Hidnert [94] have compared the average expansions of transparent and opaque rods, finding the opaque expanding the faster from about 100 to 300° where the difference is about 0.03×10^{-6}. This agrees in direction with Blackie's observations.

Hysteresis in the dilatation of vitreous silica

Although Blackie's observations, plotted in Figure XX.20, are differential, they strongly indicate a true hysteresis in the dilatation of either the one or the other specimen or possibly of both specimens of glass. A curve of this looped form could not be produced by differences in a truly reversible dilatation of the two specimens unless there were either a considerable difference in the *time-lag* of dilatation of the two, or unless there actually existed a variable difference in temperature between them. As has been shown, the time-lag or delayed dilatation is extremely small, probably of a lower order of magnitude than the differences here considered, while variable temperature-differences are excluded by the care with which Blackie's experiments seem to have been made.

The amount of the hysteresis is not known. The loop of Figure XX.20 is the resultant of two loops of unknown size and shape.

Hysteresis has also been reported by Dorsey [95] at liquid air temperatures. He found that "both specimens for about 60° on either side of —80°C [the temperature of minimum length] showed this peculiarity: above —80° when warmed they at first contracted slightly and then expanded, and when cooled they at first expanded slightly and then contracted. Just the converse of this was true for about 60° below —80°C. This could not be detected at room temperatures nor at liquid air temperatures, nor was it noticed in any other substance."

Unfortunately this evidence is not entirely conclusive as to the existence of hysteresis near —80°. An equally plausible explanation is that the effects were due to a changing temperature gradient. Such a gradient in the steel vacuum-box containing the specimen is a necessary consequence of Dorsey's method of cooling, which was wholly by conduction of heat through a steel container into the liquid air below. The reversal of the effect at —80°, its disappearance at room temperature and at liquid air temperature, and its absence from the metals and other substances studied, are all facts which fit the temperature-gradient hypothesis.

Hysteresis of the kind assumed by Dorsey would not be an unexpected phenomenon in vitreous silica, but the proof of its existence and amount is not yet sufficient.

[94] Article cited in note [60].
[95] Dorsey, H. G., article cited in note [73].

The changes in length observed by Callendar, Richardson, and others, sometimes called "hysteresis," are really observations of *permanent* changes of shape or density, due to flow of some kind, and are neither true hysteresis nor delayed dilatation (see p. 368). They are considered further in XXIV.

Delayed dilatation in vitreous silica

Although the phenomenon of delayed dilatation or time-lag is known to exist in vitreous silica, its amount is so small that it escapes any of the ordi-

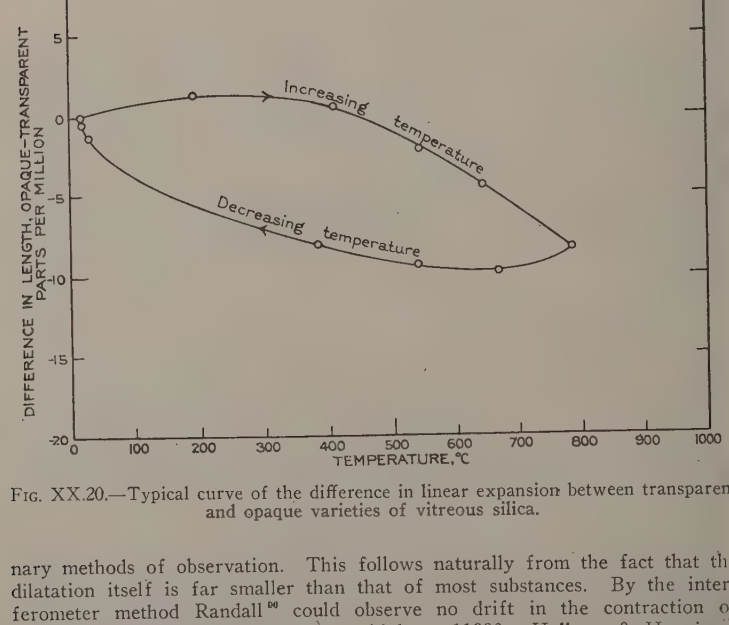


FIG. XX.20.—Typical curve of the difference in linear expansion between transparent and opaque varieties of vitreous silica.

nary methods of observation. This follows naturally from the fact that the dilatation itself is far smaller than that of most substances. By the interferometer method Randall[96] could observe no drift in the contraction of vitreous silica from temperatures as high as 1100°. Holborn & Henning[97] found no drift in the length of a 487-mm rod after 1000°; their method would have discovered an effect of 4×10^{-6} and perhaps less.

Donaldson[98] could observe no time-lag in the dilatation of the National Physical Laboratory's silica meter after comparisons with other meters at 0° to 30°. Such comparisons can be made with a precision of 0.2×10^{-6}, so

[96] RANDALL, H. M., article cited in note [65].
[97] HOLBORN & HENNING, article cited in note [67].
[98] DONALDSON, H., article cited in note [61].

that the delayed dilatation in this case, if present, must be less than $10 \times 10^{-7} t$ if t is the temperature to which the specimen has been heated.

There is a detectable time-lag, however, in the dilatation to or from temperatures of 300 to 800°, as shown by Blackie's very sensitive differential test (see p. 411).

Micro-amorphous silica

The amorphous silica obtained by calcining, at a temperature of 1000° or less, the hydrated silica precipitated by acids from solutions such as water-glass, or by the action of water on SiF_4, has an expansion coefficient which is practically the same as that of vitreous silica.[99]

Relation of specific volume to inversion-temperature

An approximate relation appears between the temperature of the inversion-point and the specific volume at the inversion-point, for the three forms cristobalite, tridymite, and quartz, if we take the lowest values of the inversion-point for cristobalite and tridymite. The relation may be expressed thus:

$$v = 488 - 0.11\, T_i$$

in which v is the kilo-volume of the form and T_i the absolute temperature of the inversion. The degree of approximation is shown in Table XX.14.

Table XX.14.

Showing Proportionality of Inversion Temperature and Specific Volume of the Three Forms of SiO_2

	T_i	v calc.	v obs.
Quartz	846	395	395
Tridymite	390	445	445
Cristobalite	473	436	436

Theory of the thermal dilatation of silica

In accordance with the theory of structure set forth in Chapter XV, the thermal changes of shape and volume of silica may be looked upon as made up of three effects:

(1) The normal thermal dilatation observed in any aggregate of molecules, by which their average distance apart is increased when their thermal vibration-amplitude increases with rising temperature.

(2) The change which takes place in the distance between two atoms accompanying that change in their relative position which culminates in the high-low inversion. A distinctive feature of this expansion is its logarithmic increase with temperature up to the final jump.

[99] Braesco, P., article cited in IV, note [14].

(3) The gradual shrinkage in volume of some unit of structure, possibly the SiO_2 atom-triplet, when certain pairs of atoms are in the high-temperature position and the temperature is rising.

Quartz

Effect (1) is subordinate in quartz. The expansion-curve of low-quartz consists mainly of effect (2), the building up toward the inversion at 573°, followed above 573° by effect (3), the thermal shrinkage of the high-configuration.

Tridymite

The low-temperature expansion of tridymite is not known, but is probably a normal thermal dilatation. The position of the oxygen atoms of low-tridymite already approximates to the high-temperature configuration, and the volume-changes at the inversions are small. At higher temperatures the shrinkage effect, effect (3), becomes the most important, and the volume tends toward constancy and may decrease. As the melting-point is approached we may expect the expansion coefficient to tend toward a positive value again.

Cristobalite

The inter-atomic distances in cristobalite are variable, and its high-low inversion is therefore spread over a range of temperature, giving a doubly-rounded form to the volume-temperature curve. At higher temperatures it is like tridymite in reaching constancy or a maximum and would probably increase again if followed to high enough temperatures.

Vitreous silica

According to the theory (Chapter XV) liquid silica is a tangle of silica threads. We thus have superposed on the structure of the atom-triplet SiO_2 another structure, though not a regular or symmetrical one. This structure is partly preserved by the rapid cooling which leads to the formation of a glass. Hence many of the interconnections of oxygen and silicon atoms are of the high-temperature configuration, even at temperatures near absolute zero.

The principal two results of this structure are, first, a negligible amount of thermal dilatation of the normal type, and, second, a shrinkage beginning at very low temperatures.

Such atomic pairs as are not of the high-temperature configuration exist with a great variety of interatomic distances, and the inversions of these pairs correspondingly occur over a wide range, beginning very low, increasing in number to a maximum, and falling off again toward

600°. The expansion accompanying the inversions accordingly first neutralizes the initial contraction, producing a minimum volume at about —80°C, then leads to an expansion which tends to fade away about 800°. The normal thermal dilatation begins to be effective now and increases until the recognizable reversible expansion is wiped out by flow of the glass.

The data on the difference in dilatation between annealed and quenched vitreous silica indicate that the quenched silica has more high-temperature atomic pairs; it has a higher dilatation at ordinary temperatures and a more marked flattening at high temperatures. This is in accord with the theory.

Historical notes

Kaye [100] seems to have been the first to observe that there is a flattening in the true dilatation of vitreous silica above 500°, and to suggest that this may have some connection with the high-low quartz inversion at 573°. He made a similar suggestion with reference to the change in relative dilatation of the transparent and translucent varieties at about 500° (see Blackie's experiments, p. 411).

Washburn [101] called attention to the analogy between water and vitreous silica, both having a temperature of minimum volume, and both, presumably, being associated liquids.

[100] Kaye, G. W. C., Phil. Mag. (1910) **20**: 718-728.
[101] Washburn, E. W., (Discussion), Journ. Amer. Ceram. Soc. (1924) **7**: 804.

Chapter XXI. THE FLOW OF THERMAL ENERGY

Substances differ greatly in their power of conducting heat from one end of a fragment to the other, just as they differ in power of conducting electricity. A quantitative measure of this property is given by the number of heat units flowing per unit of time perpendicularly across unit area within the substance, when the temperature-gradient perpendicular to the area has a constant value; this quantity is called the *thermal conductivity* of the substance. It will be stated in this chapter in 20°-gram-calories per sq. cm per second, per degree C per cm.

The thermal conductivity of a crystalline substance varies with the direction. It can be shown mathematically, assuming only that the total quantity of heat is conserved and that the conductivity is independent of the temperature, that if heat be supplied at a point within the substance the surfaces of equal temperature will be concentric ellipsoids surrounding the point. The axes of any such isothermal ellipsoid are proportional to the square roots of the thermal conductivities in three mutually perpendicular directions called the *thermic axes*. Along one of these axes the conductivity is the maximum, along another the minimum, while along the third, perpendicular to the other two, it may have an intermediate value or may be equal to the maximum or minimum.

Thermal conductivity of the forms of silica

Quartz

In accord with the symmetry of the substance, the thermic ellipsoid of low-quartz is an ellipsoid of revolution, whose axis of revolution coincides with the principal axis of the substance. It is further found experimentally that this axis is the direction of maximum conductivity.

At room temperatures the conductivity along the principal axis is about 0.029, and the conductivity perpendicular to the axis is about 0.016. The axial thermal conductivity of quartz is thus about 3.2 per cent of the thermal conductivity of copper, about twice the conductivity of mercury, and about ten times the conductivity of ordinary soft glass.

Other forms

No data are available on the thermal conductivity of tridymite or cristobalite.

The thermal conductivity of vitreous silica is about 0.003 at room temperatures. Its order of magnitude is thus about one-tenth of that of quartz, and about the same as the conductivity of most silicate glasses (range 0.0017 to 0.0028).

Variation of thermal conductivity with temperature

As a rule, substances of low thermal conductivity decrease in conductivity as the temperature rises. Quartz is no exception.

Silicate glasses, however, are an exception to this rule, and vitreous silica resembles other glasses in this respect. The thermal conductivities of quartz and vitreous silica therefore tend to approach each other as the temperature rises, the conductivity of quartz falling and that of vitreous silica rising.

At very low temperatures quartz becomes as good a conductor of heat as metallic gold is at room temperature. Vitreous silica, on the contrary, remains a poor conductor.

Table XXI.1 gives the most probable values at various temperatures.

Table XXI.1.

Thermal Conductivity of Quartz and Vitreous Silica

Temperature °C	10^3k		
	Quartz || to axis	Quartz ⊥ to axis	Vitreous
—252		680	
—250		510	ca. 1.3
—240		205	
—200	ca. 150	66	1.5
—150	74	36	2.0
—100	52	26	2.5
— 50	40	20.5	3.0
0	32	17.0	3.4
50	25.5	14.9	3.8
100	21	13.1	ca. 4.5

The experimental data on thermal conductivity

Measurements of the absolute thermal conductivity of quartz have been made by Tuchschmid (1883), Eucken (1911), and Griffiths & Kaye (1923). Vitreous silica has been measured by Eucken and by Barratt (1914). The experimental data are compared graphically in Figure XXI.1.

Tuchschmid[1] used a plate of quartz between two plates of copper. After the combination had reached a constant temperature, the lower plate—or in some cases the lower surface of the specimen itself—was suddenly cooled by a stream of water, and the difference in temperature between the upper and lower surfaces of the specimen was read at measured intervals of time. Measurements on three 3-mm plates (||, ⊥, and at 45° to the axis) yielded the following conductivities, at a mean temperature of about 12°, expressed in calories per second per degree:

|| 0.026 27; ⊥ 0.015 95; at 45 degrees, 0.021 20.

[1] Tuchschmid, A., *Das innere Wärmeleitungsvermögen von Quarz, Kalkspath und Steinsalz.* Inaug.-Diss. Zurich 1883, 48 pp.

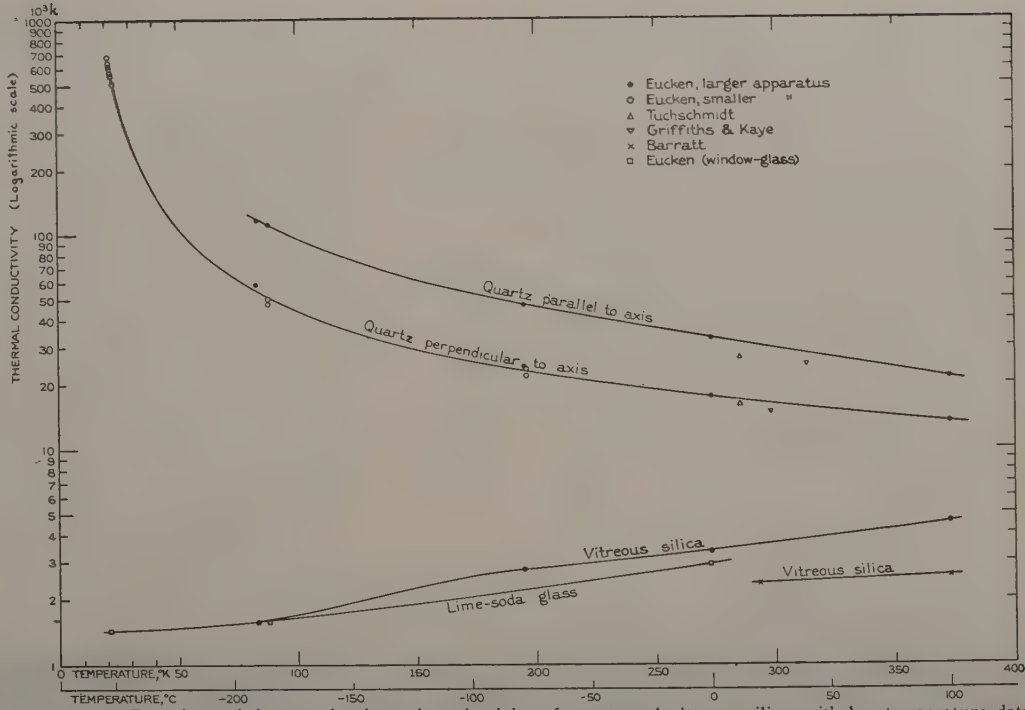


FIG. XXI.1.—Experimental data on the thermal conductivity of quartz and vitreous silica, with low-temperature data on a lime-soda glass added for comparison.

The value for the direction at 45 degrees to the axis, calculated from the other two data, is 0.0205, distinctly lower than the measured value. The reason is not known. Tuchschmid suggests that the plate may not have been cut exactly at the supposed angle.

Thermal conductivity in such materials as silica has usually been measured by the "plate method." The material to be tested, in the form of a plate, disk, or block, is placed between two good-conducting plates, to one of which heat is supplied at a constant rate while heat is withdrawn from the other. The quantities of heat flowing and the temperature gradient in the specimen are measured when a steady state of flow has been attained.

Eucken[2] determined the thermal conductivity of quartz and vitreous silica by this plate method. The amount of input of heat energy was obtained from the resistance and the voltage at the terminals of a constantan wire inclosed in a copper plate. The fall of temperature across the specimen was obtained by means of copper-constantan thermocouples.

The principal corrections were for the transfer of heat by radiation, the transfer of heat by conduction through the surrounding gas, and the thermal resistance of the layer of gas between the metal plates and the specimen. Air, hydrogen, and carbon dioxide were used in different series. The quartz and vitreous silica specimens were in the form of blocks 3 cm square and 2 to 3 cm thick.

Measurements were made at the temperatures of liquid air, ether-carbon-dioxide mixture, ice, and boiling water. The results of 43 determinations on quartz and 8 on vitreous silica are given in Table XXI.2. The accuracy appears to be of the order of 1 per cent for quartz and 2 per cent for the glass.

TABLE XXI.2.

THERMAL CONDUCTIVITY OF QUARTZ AND VITREOUS SILICA. EUCKEN.

Temperature		Conductivity in cal./sec. degree C		
°C	°K	Quartz || to axis	Quartz ⊥ to axis	Vitreous Silica
100	373	0.0215	0.013 33	0.004 57 (?)
0	273	0.0325	0.017 31	0.003 32
— 78	195	0.0467	0.024 09	0.002 77
— 185	88	0.1113	—	—
— 190	83	0.117	0.058 6	0.001 58

Eucken[3] also made a series on quartz (direction ⊥ to axis only) at the temperature of liquid hydrogen. These measurements were made with a smaller apparatus, containing a specimen in the form of a spool. The thermal junctions were placed in the cylindrical part of the spool, but since their distance apart could not be measured accurately the results were reduced to absolute measure by taking readings at 0°C and making these the basis, using the value derived from the preceding series (Table XXI.2). The results are given in Table XXI.3.

The rapid change of conductivity between 21 and 23°K is noteworthy. This change was confirmed by varying the energy input into the heating

[2] EUCKEN, A., Ann. Physik (1911) **34**: 185-221.

[3] EUCKEN, A., Verhandl. Deut. Physik. Ges. (1911) **13**: 829-835.

element. If the conductivity were only slowly changing with temperature the temperature difference between the junctions of the thermel would be proportional to the energy input. In the present case, however, the temperature differences between the junctions were found to deviate greatly from proportionality.

TABLE XXI.3.

THERMAL CONDUCTIVITY OF QUARTZ, ⊥ TO AXIS.
SMALLER APPARATUS, EUCKEN, 1911.

Temperature °K	Conductivity, cal./sec. degree C	
	First Series	Second Series
273	0.0173*	0.0173 *
196	0.0234	0.0218
88	0.0500	0.0473
23		0.51
22.3		0.56
22	0.57	
21.9		0.60
21.6	0.61	
21.4		0.64
21	0.68	

* Taken from previous measurements, as basis of comparison.

Griffiths & Kaye[4] measured the thermal conductivity of a large number of materials at room temperatures, using a plate apparatus of the kind already described. Their principal modification of the method consisted in the measurement of the heat flowing out as well as of the heat input, the outflow being obtained from the initial and final temperature of the water passing through the cold plate. This double measurement gives additional assurance against error.

Their results, obtained on quartz plates 2.53 mm thick under a pressure of 1.45 megabaryes, are:

Direction	Mean temperature °C	Conductivity cal. per sec. per °C
|| to axis	40	0.0244
⊥ to axis	25	0.0147

The accuracy is estimated to be about 1 per cent.

Data on the thermal conductivity of vitreous silica down to liquid-air temperatures have been presented in Table XXI.2. Its conductivity at lower temperatures has not been determined, but some measurements by Eucken[5] on a specimen of ordinary window glass indicate the probable course of the curve of conductivity, in view of the general similarity of behavior of vitreous silica and other silicate glasses as regards thermal conductivity. The results on window glass are:

Temperature °K	Conductivity
273	0.002 9
88	0.001 57
21	0.001 44

[4] GRIFFITHS, E., & KAYE, G. W. C., Proc. Roy. Soc. Lond. (1923) A **104**: 71-98.
[5] Article cited in note [3].

Barratt[6] measured the thermal conductivity of vitreous silica by a method somewhat similar to that of Eucken, in that the input of energy was measured electrically when the flow of heat had reached a steady state. The principal point in which Barratt's method differs from the others is in the use of a long cylindrical specimen heated at one end and surrounded by an atmosphere at constant temperature. The measurements are not absolute, but are based upon Jaeger & Diesselhorst's conductivities of lead and bismuth, rods of these two metals being used in the apparatus to establish the rate of loss of heat from the sides of the rods, which are blackened in every case.

The vitreous silica rod used was 3.32×61 mm. The results are:

Temperature	Conductivity
20°	0.002 37
100°	0.002 55

The results are considerably lower than Eucken's. The method needs to be more thoroughly tested in comparison with the better-known plate method, before the results can be given equal weight.

Measurement of relative conductivities

It is possible to determine the ratio of the two (or three) principal thermal conductivities of a crystal without measuring the absolute value of any one of them.

The simplest method of measuring this ratio is that of Senarmont. A fine hole is drilled through a thin plate of the substance to be investigated. Into this hole a wire or tube is fitted tight so that it makes good contact with the walls of the hole. When the wire or tube is heated, heat flows into the plate, distributes itself according to the thermal conductivities in various directions, and is radiated and conducted away, a steady state of flow finally being attained. If the plate has been covered with a thin sheet of wax (a method devised by Ingenhouz) the isotherm for the temperature of melting of the wax will be marked by the outer border of a circular or elliptical area within which the covering has liquefied. Surface tension will cause the formation of a slight ridge along this isotherm, so that if the plate be again cooled the maximum and minimum axes of this isothermal ridge can be measured accurately.

Senarmont[7] made 8 measurements on a plate of quartz parallel to the axis, obtaining values for the ratio between the minor and major axes of the ellipse varying from 1.25 to 1.37; mean 1.31.

Jannetaz[8] applied Senarmont's method to a large number of substances, including quartz. He introduced several modifications of the apparatus, heating some of the plates by contact with a hot point instead of by means of a rod passing through a hole. To this method of heating the objection has been made, however, that it is more likely to introduce uncertainties due to the radiation of heat from the hot point.

[6] Barratt, T., Proc. Physical Soc. London (1914) **27**: 81-92.
[7] Senarmont, H. de, Ann. Chim. et Phys. (1847) (3) **21**: 457-470, p. 464.
[8] Jannetaz, E., Ann. Chim. et Phys. (1873) (4) **29**: 5-82, pp. 45 and 73.

As the result of measurements on plates parallel to the first-order hexagonal prism $\{10\bar{1}0\}$, the trigonal prism $\{1\bar{2}10\}$, and the positive and negative rhombohedrons $\{10\bar{1}1\}$ and $\{01\bar{1}1\}$, Jannetaz could find no dissymmetry in the ellipses of conductivity, showing that the thermic ellipsoid is one of revolution about the principal axis.

Röntgen[9] made another modification in Senarmont's method by substituting for the wax a thin film of moisture such as is deposited by breathing upon a polished plate. When a hot metal point is touched to the plate a widening elliptical area is freed of film by evaporation, and its outlines can be recorded by dusting lycopodium on the plate. By this method Röntgen made 19 measurements on 2 quartz plates, obtaining values for the ratio of the axes varying from 1.337 to 1.274; mean 1.304.

Senarmont's method requires a very thin plate because there is a slight fall of temperature through the plate. Voigt[10] improved on the method by using a square plate cut into halves; one half is turned 180 degrees about an axis lying in the plate and normal to the cut, and is cemented to the edge of the other half so as to reconstitute the square plate, making an orientational twin (p. 192). When the edge of the twin-plate perpendicular to the cut is heated uniformly by contact with a body at higher temperature, the isotherm marked out by the area of melted wax shows a sharp change in direction at the cut, making an angle which depends upon the ratio of the two conductivities and the angle between the cut and the direction of maximum conductivity. Voigt also made a minor improvement by using a mixture of wax and elaidic acid, which gives a sharper boundary.

Jaeger[11] and Botez & Hertenstein[12] have made measurements on quartz by this modified method.

Table XXI.4 contains values for the ratios of thermal conductivity perpendicular and parallel to the axis obtained by the general methods just described. Ratios calculated from Eucken's direct measurements of the conductivities are also included for comparison.

It is evident that the measurement of the ratio can not be very precise, because the two conductivities vary with temperature at different rates. The apparent ratio obtained by Senarmont's method or a modification thereof must therefore vary with the temperature at the mid-point and the gradient in the plate.

Weber,[13] in 1895, published the formula: $k = 0.01576\ (1 - 0.0019\ t)$ as the thermal conductivity of quartz. As no statement is made concerning the direction of flow for which this formula holds, the result as it stands is of little value, for this conductivity is known to vary by as much as 75 per cent with the direction in the crystal. The method of measurement[14] consisted in heating a sphere, 5 to 7 cm diameter, to a uniform temperature of 100°, then placing it in rapidly moving water of constant temperature

[9] Röntgen, W. C., Ann. Physik u. Chem. (Poggendorff) (1874) **151**: 603-608.
[10] Voigt, W., Ann. Phys. u. Chem. (1897) **60**: 350-367.
[11] Jaeger, F. M., Arch. sci. phys. et nat. (1906) (4) **22**: 240-256.
[12] Botez, N., & Hertenstein, H., Physikal. Zeitschr. (1913) **14**: 332-336.
[13] Weber, R., Bull. Soc. Sci. Nat. Neuchatel (1895) **23**: 17-22.
[14] Weber, R., same (1881) **12**: 394-418.

and measuring the temperature, after a known time-interval, at the surface and center of the sphere by means of a copper-nickel thermel. Reversing the process and placing the uniformly cooled sphere in steam gave data for the conductivity at 100°.

TABLE XXI.4.

RATIOS OF THERMAL CONDUCTIVITIES PARALLEL AND PERPENDICULAR TO THE AXIS OF QUARTZ

		$\frac{\perp}{\parallel}$	$\frac{\parallel}{\perp}$
Senarmont	(1847)	0.58	1.72
Janettaz	(1873)	0.581	1.721
Röntgen	(1874)	0.588	1.701
Jaeger	(1906)	0.571	1.751
Botez & Hertenstein	(1913)	0.577 ± 0.015	1.733 ± 0.045
Eucken, 100°C	(1911)	0.620	1.613
Eucken, 0°C	(1911)	0.532	1.878

THERMAL CONDUCTIVITY OF AGGREGATES

The thermal conductivity of a crystalline aggregate, such as quartzite, sandstone, or silica brick, is less than that of the crystalline substance itself, being lowered by the resistance to flow of heat offered by (1) surfaces between crystals, (2) surfaces between crystals and air spaces, (3) the air spaces themselves.

Many measurements have been made on silica aggregates, but no attempt will be made to review them here, since the conductivity of such materials is a complex independent problem in flow of heat, and the data are only remotely related to the properties of the substance itself.

The general character of the results is indicated by the following summary of the experiments of Herschel & Lebour.[15] From their measurements it appears that the thermal resistance at the contact between quartz crystals, when they are well cemented or in cohesive contact, is not very great. A fairly dense sandstone, such as the Craigleith sandstone, conducted heat nearly as well as quartz itself. The conductivity of other, more porous, sandstones fell as low as 0.0062, about one-fifth of the axial conductivity of quartz.

Quartzite and compact sandstone are better conductors of heat than any other common types of rock. If their conductivity be taken roughly as 100, then the conductivity of granites, mica schists, and many trap rocks, is about 60; of slates and shales (across the cleavage) about 35; and of plate glass about 25.

When the grains are loose, or in cohesive contact only over very small areas, the conductivity is greatly lowered. The thermal conductivity of dry quartz sand is less than one-tenth of that of quartz.

When the air in a loose aggregate is displaced by water the thermal conductivity is greatly increased. The conductivity of wet quartz sand is of the same order as that of many sandstones and greater than that of granite.

[15] HERSCHEL, A. S., & LEBOUR, G. A., British Assoc. Rep. **1878**: 133-145; **1879**: 58-63.

Part 5. Mechanical Energy

Chapter XXII. ELASTIC PROPERTIES: VOLUME ENERGY

Reversing and non-reversing effects

It is important at the outset to distinguish between two different effects of stress, namely, the self-reversing and the non-reversing.

If after the application and removal of a pressure or a non-uniform stress the piece under investigation resumes its original properties unchanged, we may call the effect *self-reversing*. The temporary changes observed are summarized in the data and theory of *elasticity*. The elastic properties of silica are considered in this chapter and the next following.

If after the application and removal of the stress the piece remains permanently or for a long time changed in dimensions or properties, the effect will be called *non-reversing*. Such permanent changes are treated under the rubrics of *viscosity* or *fluidity, plasticity, mechanical strength*, etc. These properties of silica will be treated in Chapter XXIV.

Self-reversing effects of uniform pressure

Uniform *pressure* on an isotropic body (liquid or glass),—pressure such as is exerted by a compressed mobile liquid in which the body is immersed,—changes the volume of the body but not its shape. Uniform pressure on an aeolotropic body (a crystalline substance or a strained isotropic body) may cause a change in shape as well as in volume. This effect is analogous to that produced by uniform heating, and may be expressed as a change in axial ratios.

The change in volume is the most easily described and the best known effect, and will be considered first.

Compressibility and its quantitative statement

The most characteristic constant to use in stating the effect of uniform pressure on volume is the relative change of volume or *compressibility*, rather than the specific volume itself. The latter will vary from specimen to specimen, by amounts which though very small are yet of the same order of size as the change produced by a fairly high pressure. Nevertheless the relative change of volume due to the pressure, based on the initial volume as a reference datum, will be found the same from one specimen to another, within the limits of accuracy of the measurement.

TABLE XXII.1.

UNITS OF PRESSURE AND STRESS.

Pressures along a horizontal row in the table are equal.

Barye * (dyne per sq. cm.)	mm. mercury at 0° C and standard gravity	Pound weight per sq. in. at standard gravity	kg weight per sq. cm. at standard gravity	Megabarye or bar **	Normal atmosphere	1 km depth of rock of density 2.8†	Mile depth of rock of density 2.8†	Kilo-megabarye or kilobar
1	0.000 75	.....	.....	10^{-6}	.....	.....	.....	10^{-9}
1 333.22	1	0.019 337	0.001 3595	0.001 333	0.001 3158	.....	.....	.....
68 947.	51.715	1	0.070 307	0.068 947	0.068 046	.....	.....	.....
980 665.	735.56	14.223	1	0.980 67	0.967 84	.....	.....	.....
1 000 000.	750.06	14.504	1.019 72	1	0.986 92	.....	.....	10^{-3}
		14.696	1.033 23	1.013 25	1	.....	.....	.....
		3 982.	280.0	274.6	271.0	1	0.6214	0.2746
1 013 250.	760.	6 408.	450.6	441.9	436.1	1.6093	1	0.4419
10^9	.....	14 504.	1019.7	1000.	986.9	3.642	2.263	1

* Sometimes called a "bar."
** Sometimes called a "megabar."
† Leaving out of account the variation of gravity with depth and latitude.

The compressibility may be stated quantitatively in a number of different ways. These are analogous to the various ways of stating thermal dilatation (see XX), with the simple substitution of p for t.

The quantity which is usually measured experimentally is ΔV, the change in the total volume of the specimen, measured from some initial pressure, p_o, up to the pressure p. For purposes of comparison this must be made specific by reduction to volume-change per unit of mass or per unit of volume.

The most direct statement is of the rate of decrease of specific volume with pressure, that is, the compressibility per gram: $\beta' = -\frac{dv}{dp}$. This may be called the *true compressibility.*

For comparing the compressibility of different substances, having differing densities, it is more convenient to use the compressibility per unit volume rather than per unit mass. Since the volume varies with the pressure, there are two ways of stating the constant. We may either divide the true compressibility at pressure p by the specific volume at pressure p, giving a *true coefficient of compressibility at pressure p and temperature t:* $\beta'' = -\frac{1}{v} \cdot \frac{dv}{dp}$; or we may divide it by the specific volume at some standard pressure p_o, usually zero pressure, and at some standard temperature, usually 0°C, giving a *true coefficient of compressibility at p referred to p_o and 0°C:* $\beta = -\frac{1}{v_o} \cdot \frac{dv}{dp}$. This is the most commonly used coefficient, and is what is usually referred to by the abbreviated term, *coefficient of compressibility* or simply *compressibility.*

For convenience of calculation the compressibility is often stated in still another form, namely, as the *mean coefficient of compressibility from p_o.* This is the average compressibility per unit of pressure for the whole range of pressure from p_o to p: $\beta_m = \frac{1}{v_o} \cdot \frac{v_o - v}{p - p_o}$. When p_o is 1 atmosphere, as usual, it is practically negligible in comparison with high pressures and may be called zero, so that: $\beta_m = \frac{1}{v_o} \cdot \frac{v_o - v}{p}$.

These coefficients β, β', β'', β_m are all exactly analogous to the corresponding thermal dilatation coefficients α, α', α'', α_m (see Chapter XX).

Units

The unit of volume almost universally used is the cubic centimeter. On the unit of pressure there is not such universal agreement. The fundamental c. g. s. unit is the *barye,* which is 1 dyne per square centimeter. The most convenient multiples are the *megabarye* or bar, and the kilomegabarye, both of which will be used in this book. A megabarye is a million baryes or 10^6 dyne per sq. cm, and is very nearly the same as one atmosphere. The kilomegabarye is 1000 times larger or 10^9 dyne per sq. cm. and is convenient for very high pressures. The use of the term "bar" will be avoided, since it has acquired two different meanings and hence may cause confusion.

A comparison of pressure units is given in Table XXII.1.

Compressibilities of the forms of silica

Table XXII.2 contains the most probable values for the mean coefficient of compressibility for any random sample of quartz or vitreous silica. There are no data on tridymite and cristobalite.

Relation of compressibility to pressure

The true compressibility of low-quartz decreases by at least 15 and perhaps as much as 21 per cent between 0 and 12,000 megabaryes. In other words, the volume-decrease per megabarye becomes less as the pressure becomes greater. This behavior is similar to that of most of the other substances which have been investigated, including various metals and salts.

Table XXII.2.

Most Probable Values of the Coefficients of Compressibility of Quartz and Vitreous Silica, at Room Temperature.

$$\text{Mean coefficient } \beta_m = \frac{1}{v_0} \cdot \frac{v_0 - v}{p}.$$

$$\text{True coefficient } \beta = \frac{1}{v_0} \cdot \frac{dv}{dp}.$$

p megabaryes	Mean coefficients. $10^6\beta_m$		True coefficients. $10^6\beta$	
	Quartz	Vitreous	Quartz	Vitreous
0	2.76	2.68	2.76	2.68
2000	2.71	2.72	2.65	2.76
4000	2.65	2.76	2.53	2.84
6000	2.59	2.80	2.42	2.92
8000	2.54	2.84	2.33	3.00
10000	2.49	2.88	2.25	3.08
12000	2.44	2.92	2.18	3.16

Vitreous silica is unusual in that its true compressibility increases with pressure. The increase is of the order of 0.5 to 1.5 per cent per 1000 megabaryes, and is less at 75° than at 30°. Analogy with other silicate glasses indicates that there may be a temperature, probably above 100°C, at which the variation of compressibility would change sign, and above which the compressibility would decrease with increasing pressure, as it does in most substances.

Relation of compressibility to temperature

The true compressibility of quartz increases about 0.014 to 0.017 per cent per degree in the region between 20 and 75°C. That of vitreous silica increases about 0.11 per cent per degree in the same range of temperature.

The experimental data on compressibility

Compressibility, like thermal dilatation, can be measured directly, by the observation of volume-change under pressure. The most extensive

data of this kind for silica are the measurements of Adams, Williamson, & Johnston on quartz and of Bridgman on vitreous silica, while Madelung & Fuchs measured on both substances but at low pressures only.

Compressibility, again like thermal dilatation, can also be derived less directly from linear measurements made in one or more directions, according to the symmetry. Two directions suffice for quartz. The best measurements of this kind are by Bridgman.

Finally, the compressibility can be found indirectly from the elastic constants (see XXIII).

Agreement among the data obtained by different observers is not particularly good. Table XXII.2 is based mainly on a compromise between the results of Bridgman and those of Adams, Williamson, & Johnston, weighted somewhat by other results applying only to low pressures.

Quartz

The measurements of Adams, Williamson, & Johnston[1] were made with kerosene as the compression liquid. The quartz specimen was in the form

Table XXII.3.

Compressibilities of Silica. Adams, Williamson & Johnston, 1919.
Pressure in Megabaryes (10^6 dyne per sq. cm.)

Quartz, first series		Quartz, second series		Vitreous silica	
p	$10^6\beta_m$	p	$10^6\beta_m$	p	$10^6\beta_m$
1 960	(2.65)	2 000	(2.63)	1 960	(3.20)
2 940	2.63	3 000	2.68	2 940	3.15
3 920	2.62	4 000	2.60	3 920	3.14
4 900	2.62	5 000	2.61	4 900	3.12
5 880	2.59	6 000	2.55	5 880	3.13
6 860	2.57	7 000	2.54	6 860	3.13
7 840	2.54	8 000	2.51	7 840	3.16
		9 000	2.51		
		10 000	2.48		
		11 000	2.45		
		12 000	2.43		

of a cylinder 16×102 mm, cut from a large crystal from the U. S. National Museum. Pressures up to 12000 megabaryes were used, and were measured by means of the change in electrical resistance of "therlo" wire. The change of volume of the substance was determined between 1960 megabaryes as the minimum (p_0) and the pressure of measurement, by comparison with the volume-change of an equal volume of "soft steel" (carbon = 0.2 per cent) whose compressibility was taken as 0.60×10^{-6} at all pressures. The volume-change between 0 and 1960 was found by downward extrapolation of the curve. There was no evidence of any lag in the volume-change of quartz greater than the errors of measurement (less than 0.01×10^{-6} in β_m or β).

[1] Adams, L. H., Williamson, E. D., & Johnston, J., *The determination of the compressibility of solids at high pressures*, J. Amer. Chem. Soc. (1919) **41**: 12-42.

The results are given in Table XXII.3, stated in the form of values of β_m, which I have calculated from the published data. I have revised the results in accordance with Bridgman's recent measurements on iron,[2] which show, instead of the constancy originally assumed, a slight decrease of compressibility with pressure according to the formula (extrapolated back to 20°): $10^6\beta_m = 0.597 - 2.2 \times 10^{-6}p$.

Bridgman[3] measured the linear compressibility of quartz || and $\perp$ to the axis, at pressures up to about 12000 megabaryes. Square rods 28 mm long, cut from selected crystals, were used. The change of length of the bar was compared with that of iron as a standard, by measuring the change of electric resistance between two contacts on a nichrome wire which was fastened at one end to the specimen, while the second contact moved with the difference in linear compression between specimen and standard. The compressibility of the iron standard was separately determined in absolute measure.[4] Readings were made at two temperatures, 30 and 75°C.

TABLE XXII.4.

LINEAR COMPRESSIBILITIES OF QUARTZ. BRIDGMAN, 1925.

Pressure		$10^6\gamma_{m\parallel}$		$10^6\gamma_{m\perp}$		$10^6\beta_m$	
kg/sq. cm	Megabaryes	At 30°	At 75°	At 30°	At 75°	At 30°	At 75°
0	0	(0.753)	(0.764)	(1.072)	(1.076)	(2.90)	(2.925)
2 000	1 961	0.734	0.745	1.041	1.046	2.823	2.849
4 000	3 923	0.716	0.724	1.012	1.010	2.751	2.759
6 000	5 884	0.695	0.702	0.976	0.978	2.663	2.673
8 000	7 846	0.673	0.678	0.946	0.952	2.584	2.603
10 000	9 807	0.653	0.661	0.931	0.935	2.538	2.555
12 000	11 768	0.636	0.644	0.922	0.928	2.505	2.527
Average percentage deviation from smooth curve		0.24	0.16	0.09	0.08		

I have recalculated the published results and expressed them in Table XXII.4 as mean coefficients of linear compression, $\gamma_{m\parallel}$ and $\gamma_{m\perp}$: $\gamma_m = -\frac{1}{p} \cdot \frac{\Delta l}{l_o}$, where Δl is the change in length of a bar which has the length l_o at zero pressure and 0°C; and p is the pressure in megabaryes. The last two columns contain values of β_m calculated from $\gamma_{m\parallel}$ and $\gamma_{m\perp}$.

The compressibilities of quartz and vitreous silica have been determined at lower pressures by Mädelung & Fuchs.[5] They used a glass "piezometer" containing mercury, with a capillary tube on which the change of volume of the specimen was read. The piezometer and capillary were inclosed in a pressure vessel with a reentrant heavy glass tube through which the capillary

[2] BRIDGMAN, P. W., Proc. Amer. Acad. Arts & Sci. (1923) **58**: 163-242.

[3] BRIDGMAN, P. W., *Linear compressibility of fourteen natural crystals,* Amer. J. Sci. (1925) (5) **10**: 483-498.

[4] Article cited in note [2].

[5] MADELUNG, E., & FUCHS, R., *Kompressibilitätsmessungen an festen Körpern,* Ann. Physik (1921) (4) **65**: 289-309.

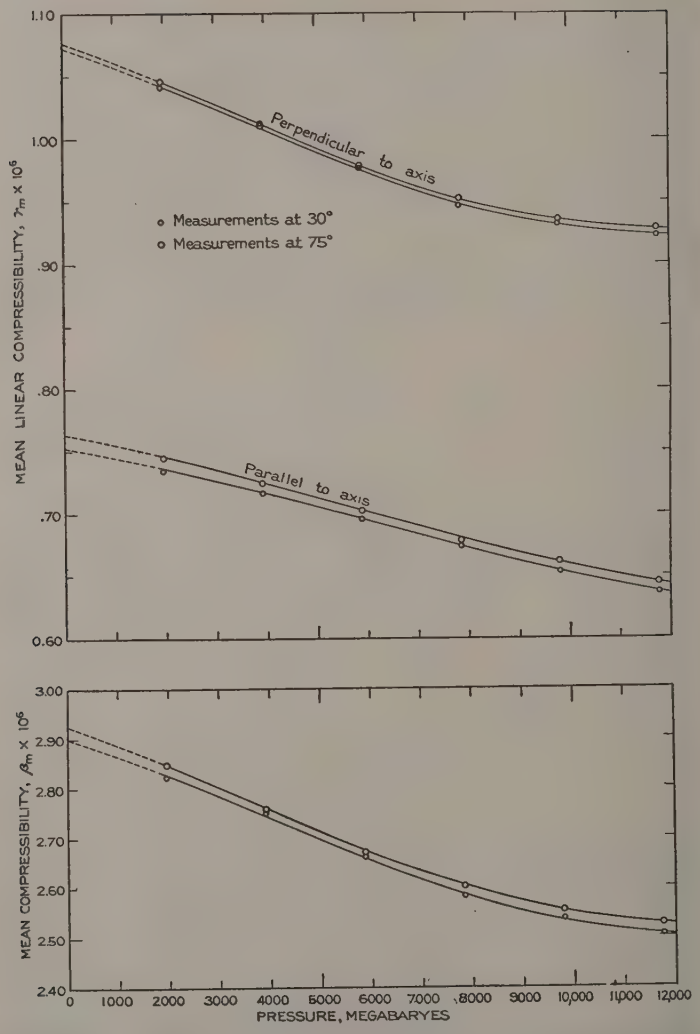


FIG. XXII.1.—Mean linear and volumetric coefficients of compressibility for quartz, referred to $p = 0$ and $t = 0°C$. From data of Bridgman, 1925.

could be seen. With this apparatus they measured the mean compressibility to 149 megabaryes, at 0°C. Specimens weighing from 8 to 10 grams were used. The results on silica are:

Material	Source	$10^6\beta_m$	
Quartz crystal	Madagascar	2.65 ± 0.02	
" "	Striegau	2.65 ± 0.02	
" " *	Unknown	2.67 ± 0.02	2.68
" " *	"	2.73 ± 0.02	
Vitreous silica	Heraeus' works	2.69 ± 0.02	

* First dipped in paraffin to seal cracks. Compressibility of paraffin was determined and corrected for.

The basis of these values is the figure 3.860×10^{-6} for the compressibility of mercury under the same conditions. Since the piezometer measures the difference in compressibility between mercury and the substance, any change in the value adopted for mercury requires an equal (not proportional) change in the value of β_m for quartz or vitreous silica.

Adams, Williamson, & Johnston's results on quartz are fairly expressed by the linear formula: $10^6\beta_m = 2.70 - 22 \times 10^{-6}\ p$. The corresponding true compressibility at pressure p would therefore be given by: $10^6\beta = 2.70 - 44 \times 10^{-6}\ p$. Bridgman found that a linear formula of this kind would not express his results within the limit of error, since the departure of the linear compression from proportionality to the pressure was not parabolic. The departure was considerably larger for the equatorial (perpendicular) direction than for the axial.

Furthermore, there is a slightly reversed curvature between 8000 and 12000 megabaryes. This means that within this range the true axial linear compressibility increases with pressure, a rather unusual behavior.

The compressibility of quartz can be calculated from its 6 elastic constants (see XXIII). These have been determined by Voigt. The compressibility derived from his data, in terms of the megabarye as unit of pressure, is 2.646×10^{-6}, which is in fairly good agreement with the value 2.68 as measured at low pressures, and with the value 2.70 at zero pressure extrapolated from the data of Adams, Williamson, & Johnston. It is considerably lower than Bridgman's value.

The various values of compressibility at zero pressure and room temperature are collected and compared below:

Author	$10^6\beta_m$
Bridgman	2.89
Adams, Williamson & Johnston	2.70
Madelung & Fuchs	2.68
Voigt	2.65

Although Bridgman's work is of considerably higher precision than that of either Adams, Williamson, & Johnston or Madelung & Fuchs, it should be noted that the compressibility derived therefrom is an indirect result, and so of less weight than the direct measurements. Nevertheless there is no obvious reason for the large deviation of his result from the other three values.

Bates[6] measured one of the two linear components of the compressibility of quartz, namely, that in the direction of the axis,[7] by an interferometric method. The plane parallel faces of a cylinder 12.48 mm long and 22.20 mm in diameter were half-silvered, and the change in their distance apart was determined by the movement of the interference bands formed in light sent through the cylinder. The compression was produced by means of gas pumped into a brass cylinder with quartz windows, and was therefore uniform in all directions.

Measurements were made over a range of 170 megabaryes. The compressibility in the axial direction was found to increase with the pressure. The linear compressibility[8] at 62 megabaryes is 0.591×10^{-6}, and at 173 mb. is 0.754×10^{-6}. The published value for 18.5°C and 150 mb. is 0.753×10^{-6}.

The change with pressure seems abnormally large, and moreover is in the opposite direction to that found at high pressures. Since the effects measured are very small, the apparent increase may be due to experimental error. The axial compressibility at 173 mb., however, agrees fairly well with Bridgman's determinations.

It is just possible that there actually is an increase in the compressibilities at low pressures, changing to a decrease as the pressure becomes greater; this would explain why the values of Bridgman and of Adams, Williamson, & Johnston are higher than those of Voigt and of Madelung & Fuchs.

Vitreous silica

The data of Adams, Williamson, & Johnston on vitreous silica have already been presented in Table XXII.3. The data are not as accurate as their measurements on quartz, because the specimen used was in the form of a capillary tube of 1 mm bore and 18 mm outside diameter, and contained numerous fine thread-like bubbles not open to the outside. Its density was about 3 per cent below normal, probably on account of the bubbles. Their effect on the compressibility is unknown, but may be expected to make the compressibility appear too high by an amount something less than 3 per cent. The compressibility appeared to be constant within this limit of accuracy, at about the value 3.1×10^{-6}.

Better data have since been obtained by Bridgman.[9] The measurements were linear, made over the range 1000 to 12000 megabaryes, by the method already described, on a rod of clear vitreous silica about 160×6 mm obtained from the General Electric Company (Lynn). The results, in the form of the mean coefficient of compressibility referred to zero pressure and 0°C, can be expressed within the limit of error by the linear equations:

$$10^6\beta_m = 2.699 + 18.3 \times 10^{-6}p \quad \text{at } 30°$$
$$10^6\beta_m = 2.829 + 7.46 \times 10^{-6}p \quad \text{at } 75°$$

[6] Bates, H. C., *On the compressibility of solids by an interferometer method*, Trans. Roy. Soc. Canada (1923) **17**, III, 93-101.

[7] According to data obtained by correspondence with Mr. Bates.

[8] According to data obtained by correspondence with Mr. Bates.

[9] Bridgman, P. W., *The compressibility of several artificial and natural glasses*, Amer. J. Sci. (1925) (5) **10**: 359-367.

There was no detectable lag in the volume-change nor any permanent change of volume.

Schidlof & Alfthan-Klotz[10] measured the change of volume of one cylindrical and two spherical bulbs of transparent vitreous silica filled with mercury, under interior and exterior pressures of 3 to 5 megabaryes, and also the compressibility of the walls themselves under similar pressures, by noting the movement of the mercury in capillaries attached to the bulbs. The two values of $10^6\beta_m$ obtained were 2.32 and 1.90, with a somewhat uncertain error due to air bubbles adhering to the walls. The extremely small effect obtainable at such low pressures makes the accuracy of the measurement doubtful.

Madelung & Fuchs' measurement has already been described.

The data on compressibility of vitreous silica at zero pressure and room temperature may now be compared:

Author	$10^6\beta_m$
Adams, Williamson, & Johnston	3.1 (specimen unsatisfactory)
Madelung & Fuchs	2.69
Bridgman	2.67
Adams & Gibson[11]	2.64
Schidlof & Alfthan-Klotz	2.1 (method unsatisfactory)

The foregoing direct determinations may also be compared with the following, derived indirectly from measurements of elasticity (see Table XXIII.3):

Schulze	2.35
Heymans & Allis	3.15
Stumpf	3.13
Boys	2.15

The agreement among these indirect results, and also between these and the direct measurements, is not very good. The reason for the discrepancies will not be found until some investigator makes a careful study of the degree of constancy of the elastic constants in different kinds of specimens, and also their variation with stress when the stresses are relatively small. The variation with temperature is also large enough to require attention.

[10] Schidlof, A., & Alfthan-Klotz, Arch. sci. phys. nat. (1909) (4) **27**: 487-516.

[11] From a preliminary examination of unpublished data obtained at the Geophysical Laboratory.

Chapter XXIII. ELASTIC PROPERTIES: ENERGY OF FORM

The self-reversing effects of stress

The effects of external stress, such as tension, non-uniform compression, or torsion, upon an elastic solid are complex and difficult to describe, partly because they are so imperfectly known. The dividing line between the self-reversing and the non-reversing effects (see p. 424) is itself rather hazy, and as increased precision of measurement narrows the limits within which no permanent effects remain visible, the truly self-reversing effects seems sometimes but an ideal limit to a series of actual effects which are all non-reversing. Nevertheless, the distinction is useful, both in experiment and in theory.

Elastic constants

In general, the effect of an external force of any kind is to produce at any given point in the body a *strain.* This strain may be described as the change in length and direction of the short line joining any two points which are very near together. The strain may be resolved into 6 components, of which 3 are changes in length, or *extensions,* and 3 are changes in direction, or *shearing strains.*

At the same time, there is produced at the point in question a state of *stress,* a force per unit area considered in all possible directions around the point, and this stress also may be resolved into 6 components.

In the most general case (a triclinic crystal, for example) it is necessary to know *21 elastic constants,* because the 6 components of strain must be combined with the 6 components of stress in 21 independent pairs $(6 + 5 + 4 + 3 + 2 + 1)$ in order to obtain the complete set of relations between stresses and strains.

For crystals of higher and higher symmetry the number of necessary constants becomes progressively smaller, until for a homogeneous isotropic non-crystalline solid only 2 constants are necessary.

It should be noted that the complete set of relations, involving the 21 constants referred to above, is based on the assumption that each component of stress can be expressed as a linear function of the 6 components of strain. Furthermore, the axes of coordinates are usually so chosen as to fit the axes and planes of symmetry of the substance under investigation. The 21 constants c_{11}, c_{12}, c_{13}, c_{14}, c_{15}, c_{16}; c_{22}, c_{23}, c_{24}, c_{25}, c_{26}; c_{33}, c_{34}, c_{35}, c_{36}; c_{44}, c_{45}, c_{46}; c_{55}, c_{56}; and c_{66} are then known most logically as the *principal elastic moduli*[1] of the substance.

[1] Usage as to the meanings of these terms, unfortunately, varies. Auerbach's usage for "modulus" is followed in this book. Voigt calls c_{11}, etc., "Elastizitätskonstanten," and s_{11}, etc., "Elastizitätsmoduln." I shall call c_{11}, etc., the "moduli"; s_{11}, etc., the "coefficients"; and shall refer in a general way to any of these as "constants."

If each component of stress is a linear function of the 6 components of strain, as assumed above, then each component of strain is a linear function of the 6 components of stress. This gives us another set of 21 constants, which are calculable from the first set, and which will be called the *principal elastic coefficients*.[1] They are usually expressed by the symbols s_{11}, s_{12}, etc.

General character of the elastic constants of the modifications of silica

The least symmetrical modifications of silica are low-tridymite (orthorhombic) and low-cristobalite (orthorhombic or tetragonal). 9 constants are necessary to describe completely the changes in shape and volume of an orthorhombic crystal under stress.

The high-tridymites are hexagonal or trigonal, requiring, at most, 7 constants, and possibly as few as 5. High-quartz is hexagonal trapezohedral, requiring 5 constants. Low-quartz is trigonal trapezohedral and requires 6 constants. High-cristobalite is isometric and requires 3.

Vitreous silica, if truly isotropic, would require but two constants to define its elastic behavior.

Of the forms of silica only two, quartz and vitreous silica, have been investigated experimentally.

Elastic constants of vitreous silica

Vitreous silica, being the simplest,—at least in theory,—will be discussed first.

Fundamental constants of an isotropic substance

The experimental results of the stretching of rods, twisting of fibers, bending of bars and plates, etc., can be stated in a variety of ways as constants independent of the particular dimensions of the specimen. But since, as we have seen, only two constants are needed to describe the elastic behavior of an isotropic non-crystalline solid, only two out of such a group of constants are truly independent.

The gradual reduction in the number of necessary elastic constants, in a series of substances of increasing symmetry, brings us finally in the case of an isotropic substance to the 2 constants: c_{11} and c_{12}. They are the constants which relate the stress on any small element of area within the substance to the two displacements, normal and tangential, which accompany that stress.

Various other constants can be defined and experimentally determined. If any two of them are known, all the others, including c_{11} and c_{12}, are calculable from the first two.

The two which are adopted in this book as fundamental are

(1) The *modulus of compression*, K
(2) The *modulus of rigidity*, R

The modulus of compression is the reciprocal of the true coefficient of compressibility, already described in Chapter XXII: $K = \frac{1}{\beta''}$. The modulus of rigidity is still to be considered. It may be defined experimentally by the formula: $R = \frac{\pi r^4}{lfa}\theta$, in which r is the radius and l the length of a cylindrical bar of the substance, which is held fast at one end, while a twist of angular magnitude θ is given to the other end by two equal and opposite forces f acting on the ends of an arm of length a which is fastened by its middle point to the axis of the cylinder. The cylinder is assumed to be long enough to make end-effects negligible.

TABLE XXIII.1.

INTERRELATIONS BETWEEN ELASTIC CONSTANTS OF AN ISOTROPIC SOLID.

(Constants at the left are expressed in terms of the constants at the top of the table.)

	c_{11} and c_{12}	K and R	E and σ	E and R	β''
$c_{11} =$		$-(K + \frac{4}{3}R)$	$-E\frac{1-\sigma}{(1+\sigma)(1-2\sigma)}$	$\frac{R(E-4R)}{3R-E}$	
$c_{12} =$ (or $-\lambda$)		$-(K - \frac{2}{3}R)$	$-E\frac{\sigma}{(1+\sigma)(1-2\sigma)}$	$\frac{R(2R-E)}{3R-E}$	
$K =$	$-\frac{1}{3}(c_{11} + 2c_{12})$		$\frac{E}{3(1-2\sigma)}$	$\frac{ER}{3(3R-E)}$	$\frac{1}{\beta''}$
$R =$	$-\frac{1}{2}(c_{11} - c_{12})$		$\frac{E}{2(1+\sigma)}$		
$E =$	$\frac{(c_{12}-c_{11})(c_{11}+2c_{12})}{c_{11}+c_{12}}$	$\frac{9KR}{3K+R}$			
$\sigma =$	$\frac{c_{12}}{c_{11}+c_{12}}$	$\frac{3K-2R}{2(3K+R)}$		$\frac{E-2R}{2R}$	
$E' =$			$\frac{E}{1-\sigma^2}$		

DERIVED CONSTANTS OF AN ISOTROPIC SUBSTANCE

Other moduli and constants in common use, but logically secondary in character and calculable from c_{11} and c_{12} or from K and R are the following:

(3) The modulus of elasticity or *Young's modulus*, E. In general terms, it is the weight per unit cross-section required to stretch a vertically suspended rod by a definite, and very small, fraction of its length. Otherwise stated, it is the ratio of stress to stretch.

The statement that Young's modulus for vitreous silica is 700 kilomegabaryes means that a vertical rod, 1 sq. cm in cross-section, would be lengthened to the extent of 0.001 of its length by a stress of 700 megabaryes, or by a suspended weight of 714 kilograms.

(4) The elasticity-number or *Poisson's ratio*, σ. It is definable experimentally as the ratio between the lateral contraction in diameter and the longi-

tudinal extension in length of the rod referred to under (3). It is the ratio of pinch to stretch.

(5) *Modulus of penetration, E′.* The modulus of penetration[2] may be defined as π times the theoretical pressure existing at the center of the surface of contact of two pieces of the material being tested (one of which had originally a spherical surface, of radius 1, while the other had originally a plane surface) at the moment when the two have been so pressed together that the radius of the surface of contact is 1.

Since the pressure at the center is theoretically 3/2 of the average pressure over the contact-surface, the modulus is defined experimentally by the formula: $E' = 12\,\rho\,\frac{p}{a^3}$ in which ρ is the radius of curvature of the originally spherical surface, p is the total load, and a is the diameter of the contact-surface.

The modulus of penetration is theoretically related to Young's modulus and Poisson's ratio thus: $E' = \frac{E}{1-\sigma^2}$. The theory of this modulus is not entirely satisfactory and it is therefore not usually included with the better-known moduli.

Some interrelations among the constants are assembled in Table XXIII.1, adapted from a table by Auerbach.

Summary of the elastic constants of vitreous silica

The most probable values of the elastic constants of any random specimen of vitreous silica, as determined experimentally, are given in Table XXIII.2.

The values given are not theoretically consistent throughout. In a later section will be found maximum and minimum values as actually determined, and a comparison of these with values calculated from other pairs of constants. A study of the assemblage as a whole will show that there is not much consistency, either in theory or experiment, among these various values. Part of the reason, I feel sure, is that the usual specimen of vitreous silica is not structurally isotropic, as we have been assuming, but is to a greater or less degree aeolotropic.

Table XXIII.2.

Elastic Constants of Vitreous Silica.

The unit is the kilomegabarye (10^9 dyne per sq. cm.).

Modulus of compression	K	370
Rigidity	R	305
Young's modulus	E	700
Poisson's ratio	σ	0.14
Modulus of penetration	E'	690

The effect of a change of temperature on the elastic constants of vitreous silica is only imperfectly known; the rigidity is the only constant

[2] Hertz, H., Verh. Physik. Ges. Berlin (1882) 1: 67; Verh. Ver. z. Beförd. Gewerbfl. (1882) 61: 449-463. Auerbach, F., Ann. Physik. u. Chem. (1892) 45: 262- 276.

whose change with temperature has been measured over any considerable range.

The rigidity of vitreous silica increases with the temperature, over the entire range from the boiling point of liquid air to about 880°C, where the rigidity reaches a maximum. It then falls rapidly, approaching zero not far above 1000°.

A rigidity increasing with temperature is unusual, since the effect in ordinary silicate glasses and in metals is a decrease with rising temperature.

TABLE XXIII.3.

EXPERIMENTAL DETERMINATIONS OF VARIOUS ELASTIC CONSTANTS OF VITREOUS SILICA AT ROOM TEMPERATURE, REDUCED TO KILOMEGABARYES (10^9 DYNE PER SQ. CM).

(Constants in parentheses are calculated from the experimentally determined constants.)

Author	Form of specimens	Method	K	E	R	σ
Schulze	Bar	Acoustic vibrations	(425)	612	243	(0.260)
Heymans & Allis	Bar	Bending	(317)	689	(303)	0.138
Lees, Andrews & Shave	Bars	Bending		400		
Stumpf	Bars	Bending and torsion	(319)	699	308	(0.133)
Schidlof & Alfthan-Klotz	Bulbs	Compression	474	612	(234)	(0.306)
Adams & Gibson	Bar	Compression	379			
Bridgman	Rod	Compression	374			
Madelung & Fuchs		Compression	372			
Auerbach	Plates (?)	Hardness		(711)		
Threlfall	Fibers	Bending and torsion	(144)	518	288	(–0.10)
Boys	Fibers	Bending (?) and torsion	(418)	600	238	(0.26)
Horton	Fibers	Torsional oscillation			300	
Barnett	Fibers	Torsional oscillation			146	
Guye & Fréedericksz	Fiber	Torsional oscillation			226	

THE EXPERIMENTAL DATA ON THE ELASTIC CONSTANTS OF VITREOUS SILICA

We have already seen (VIII) that vitreous silica may be constitutionally aeolotropic (non-isotropic) as shown by examination in polarized light. In Chapter XVIII we have seen that the density of vitreous silica is more variable than is the density of quartz. Furthermore, the glass is quite frequently optically aeolotropic even when it appears to be chemically or constitutionally homogeneous.

It is not surprising, then, to find that the published values for the elastic constants of vitreous silica do not agree very well. The disagreements are due partly, no doubt, to optically visible strain in some of the specimens used. This is particularly true of drawn fibers or rods, and of

blown bulbs. But even with this variation eliminated it is likely that different specimens will not agree within the limits of error of the methods, because the personal idiosyncrasies of such a material seem to stand out more strongly in its elastic behavior than in any other of its properties.

The principal experimental determinations are summarized in Table XXIII.3. The determinations on which K alone is based have already been discussed in Chapter XXII. It remains to consider the original experimental data on the other constants.

The investigations are readily classified according to the number and kind of constants determined.

Measurements of the two fundamental constants E and R at the same time have been made by Gibson & Gregory (1889), Threlfall (1890), Schulze (1904), and Stumpf (1913); K and E by Schidlof & Alfthan-Klotz (1909); E and σ by Heymans & Allis (1923). R alone was measured by Barnett (1898), Horton (1905), and Guye & Fréedericksz (1910); E alone by Lees, Andrews, & Shave (1924).

Rigidity

The most precise measurements of rigidity of vitreous silica are those of Horton.[3] He used the method of oscillations of loaded fibers, measuring the time by Poynting's method of coincidences, good to about 1 in 100,000 in this case. He also improved greatly the accuracy of measurement of the diameter by dividing the fiber into 10 to 12 pieces and counting the number of rotations when each piece was rolled for a known distance between two small glass tubes. Most of the fibers were found to be slightly conical but the variation from end to end was usually less than 1 per cent. The precision of the measurements of the diameter was 1 in 100,000.

The results at 15° are given in Table XXIII.4.

Horton observed that the period of oscillation was independent of the amplitude, up to at least 10 degrees, or about 0.7 degree per cm of length.

TABLE XXIII.4.

MODULUS OF RIGIDITY, R, OF VITREOUS SILICA FIBERS AT 15° C. HORTON, 1905.

No.	Diameter μ	Length mm	R Kilomegabaryes
6	10.256	136.055	304.2 †
3	11.422	145.05	298.6
2	11.938	148.645	278.8 *
5	14.156	143.38	299.2 †
1	21.160	112.68	296.5
4	22.478	140.49	301.8 †
			Mean* 300.1

* Diameter of No. 2 irregular; not included in mean.
† Previously heated several times to 100°.

[3] HORTON, F., Philos. Trans. Roy. Soc. Lond. (1905) **A 204**: 407-431.

Boys[4] states that the rigidity of vitreous silica in the form of a fiber is influenced by the tension on the fiber. Horton's measurements on 6 fibers (p. 439) show that a change of tension from 670 to 3200 megabaryes has no recognizable influence on the rigidity, but the tensions used by Boys were probably much greater than this. Edwards, Bowen, & Alty,[5] after measuring the effect of tension on the rigidity of metallic wires, could find no such effect in a silica fiber, but give no quantitative data on silica.

Measurements of rigidity by the method of torsional oscillations have also been made by Gibson & Gregory,[6] by Threlfall,[7] by Barnett,[8] and by Guye & Fréedericksz.[9] Boys does not report the individual determinations but states that the rigidity differed greatly from fiber to fiber, the value published being 238. Threlfall made measurements on 4 fibers of diameter 8 to 25 μ; Barnett, on 6 fibers of diameter 27 to 49 μ, but relatively short (30 to 45 mm); and Guye & Fréedericksz, 1 fiber of diameter 612 μ. The results are assembled in Table XXIII.5.

TABLE XXIII.5.

RIGIDITY OF VITREOUS SILICA (IN THE FORM OF FIBERS) AT ROOM TEMPERATURE.

	Temp. °C	Diameter μ	Rigidity Kilomegabaryes	
Gibson & Gregory (Boys)	Not stated	Not stated		238
Threlfall	23	7.75	289	288
	23	9.27	212	
	22	21.14	342	
	24	24.55	310	
Barnett	Not stated	26.6 to 27.2	141	146
	"	34.6 to 35.2	167	
	"	38.7 to 40.2	151	
	"	38.4 to 41.8	149	
	"	38.9 to 42.3	141	
	"	43.6 to 49.0	125	
Guye & Fréedericksz	0	612		225.5

Schulze[10] determined two elastic constants of vitreous silica by measuring the vibration tones of the bending and torsional vibrations of a square bar of the glass. He found that a bar $2.72 \times 10 \times 100$ mm had a second transversal tone of 2048 on a length of 84.0 mm and a first torsional tone of 5307 on a length of 74.5 mm. The combination of these two data with the density gives the values:

$$E = 611.7 \text{ kilomegabaryes}$$
$$R = 242.7 \text{ kilomegabaryes}$$
$$\sigma = 0.260$$

[4] Boys, C. V., Phil. Trans. Roy. Soc. Lond. (1895) **186**: 65.
[5] Phil. Mag. (1926) (7) **2**: p. 338.
[6] Reported by Boys, C. V., J. Soc. Arts (1889) **37**: 815-822, 827-836, 839-845, 852-860.
[7] THRELFALL, R., Phil. Mag. (1890) **30**: 99-116.
[8] BARNETT, S. J., Physical Rev. (1898) **6**: 114-120.
[9] GUYE, C. E., & FRÉEDERICKSZ, V., Arch. sci. phys. nat. (1910) (4) **29**: 49-61, 157-174, 261-289, esp. p. 284.
[10] SCHULZE, F. A., Ann. Physik (1904) **14**: 384-388.

An uncertainty in this method arises from the problem of a firm clamp for the bar.[11] The true length of the vibrating part may thereby be left in doubt, and an unknown error be introduced into the elastic constants.

Stumpf[12] made two series of careful measurements on 4 bars of vitreous silica $1.4 \times 6 \times 80$ mm, cut from a plate made by Heraeus, and showing practically no strain. The dimensions of each were measured at several points to 0.001 mm. Both bending (by central load) and torsion experiments were made, the deformations being measured by means of light reflected from mirrors attached to the bars. The results are given in Table XXIII.6. Each value is an average of several determinations on different lengths and with different loads.

With double weight given to the second series as the more reliable, the final averages are:

$$E = 698.5 \text{ kilomegabaryes}$$
$$R = 308.4 \text{ kilomegabaryes}$$
$$\sigma = 0.133$$

TABLE XXIII.6.

EXPERIMENTAL DATA ON YOUNG'S MODULUS (E) AND RIGIDITY (R) OF VITREOUS SILICA. STUMPF, 1913.

Unit of pressure is kg per sq. mm.

Bar No.	E		R	
	Series I	Series II	Series I	Series II
1	7090	7131	3163	3133
2	7310	7113	3170	3141
3	7060	7119	3190	3163
4	7070	7137	3230	3162

Young's modulus

In connection with his measurements of rigidity, Threlfall[13] determined Young's modulus by the bending of cylindrical fibers, with the following results:

Diameter in μ	E, kilomegabaryes
55.93	581.6
61.02	760.9
83.75	417.9
87.71	412.6
Same	416.3
Mean	517.9 at 23°

Heymans & Allis[14] determined Young's modulus and Poisson's ratio by bending experiments on a bar of vitreous silica (from the General Electric

[11] STUMPF, p. 880 of article cited below.

[12] STUMPF, F., *Die elastischen Konstanten von Quarzglas*, Ann. Physik (1913) (4) **40**: 879-886.

[13] Article cited.

[14] HEYMANS, P., & ALLIS, W. P., J. Math. Phys., Mass. Inst. Techn. (1923) **2**: 216-233.

Company, Lynn). The apparatus was arranged with two pairs of knife-edges to give a pure bending stress to the bar, and its longitudinal curvature as well as its transverse curvature were measured by means of the hyperbola-shaped interference bands formed between the upper surface of the bent bar and an optically flat plate laid on the bar. The maximum stress f is calculated by

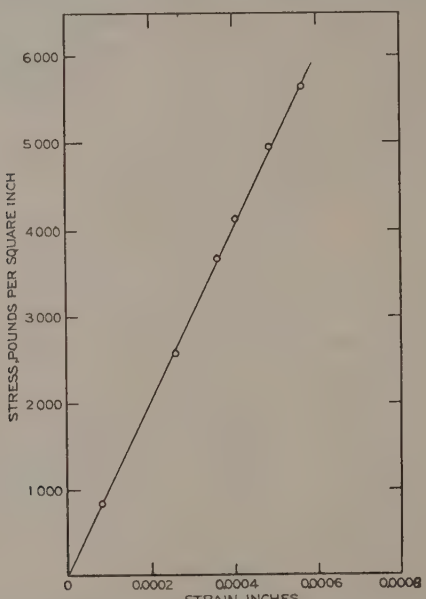


FIG. XXIII.1.—Experimental data on the relation between stress and strain in a bent bar of vitreous silica. Heymanns & Allis, 1924.

the formula: $f = \frac{6M}{bh^2}$, in which M is the bending moment, b the width of the bar, and h the height of the bar. The elongation was computed from the curvature.

The measured relation between stress and strain so obtained is shown in Figure XXIII.1 (length of bar not stated). The graph is a straight line, and the value of E is 689 kilomegabaryes.

The lateral change of dimensions was computed from the transverse curvature, giving $\sigma = 0.138$.

From their measurement of the change of volume of silica bulbs, combined with the lower of their two measurements of the compressibility of the glass itself, Schidlof & Alfthan-Klotz [15] deduced the following constants:

[15] Article cited in XXII, note [10].

$E = 612$ kilomegabaryes
$R = 234$ kilomegabaryes
$\sigma = 0.306$

The measurements of Lees, Andrews, & Shave[16] were intended to show the effect of temperature on Young's modulus, and are not of high accuracy

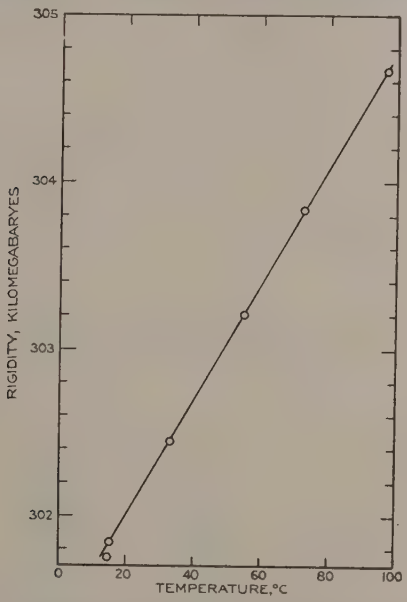


FIG. XXIII.2.—Change of rigidity of vitreous silica fiber with temperature. Data of Horton, 1905.

as absolute measurements. The values at 20°, as deduced from the smoothed curves of Figure XXIII.4, are:

	Kilomegabaryes
Rod (1)	400
Rod (3)	350
Rod (3) reheated	520
Rod (3) rotated 90° in clamp	340
Rod (3) again reheated	395
Mean	400

The modulus of penetration of vitreous silica has been measured only by Auerbach, who obtained the value 697 kilomegabaryes. This corresponds to a value for E of 711.

[16] Article cited in note [26].

Experimental data on the change of rigidity of vitreous silica with temperature

The most precise measurements of the change of rigidity of vitreous silica with temperature are those of Horton. They also cover the widest range of temperature, 20 to 1058°. The range below 0°C has been studied by Guye and his collaborators, while experiments on the temperature coefficient of rigidity between room temperature and 100° have been made by Threlfall and by Barnett.

Horton[17] measured the rigidity by the method of torsional oscillations at 5 temperatures between room temperature and 100°. The results, as given in Table XXIII.7 and plotted in Figure XXIII.2, show that the relation between rigidity and temperature is very nearly linear, especially if the value taken at room temperature is that following the first heating. The rigidity at 15° showed a small but permanent increase after the fiber had been at 33° or higher for several hours.

TABLE XXIII.7.

CHANGE OF RIGIDITY OF A VITREOUS SILICA FIBER WITH TEMPERATURE, AND SMALL VARIATIONS IN ITS RIGIDITY WHEN MAINTAINED AT A CONSTANT TEMPERATURE. HORTON, 1905.

Date	Temperature °C	Rigidity Kilomegabaryes	Time during which temperature had been maintained Hours
25 Mar.	14.87	301.754	...
26 Mar.	14.67	301.759	...
26 Mar.	33.14	302.456	2.75
26 Mar.	33.22	302.454	5.00
26 Mar.	33.45	302.445	7.75
27 Mar.	14.88	301.783	...
27 Mar.	54.44	303.192	3.75
27 Mar.	55.02	303.205	6.00
27 Mar.	55.20	303.243	8.30
28 Mar.	15.46	301.843	...
28 Mar.	72.47	303.834	3.55
28 Mar.	72.67	303.827	6.20
28 Mar.	72.78	303.845	8.75
29 Mar.	16.30	301.879	...
29 Mar.	97.38	304.687	3.10
29 Mar.	97.39	304.674	5.55
29 Mar.	97.41	304.678	8.00
30 Mar.	14.80	301.833	...
30 Mar.	97.06	304.660	2.50
30 Mar.	97.13	304.672	4.75
31 Mar.	15.37	301.841	...
20 Apr.	15.90	301.874	...
20 Apr.	97.67	304.715	3.00
20 Apr.	97.69	304.689	5.55
20 Apr.	97.77	304.676	8.00
21 Apr.	14.98	301.845	...

[17] Article cited in note [3].

Horton's measurements of the temperature coefficient of rigidity for different fibers, between room temperature and 100°, yielded the following results:

Diameter μ	Temperature coefficient $\times 10^6$
22.478	114.6
14.156	115.2
10.256	140.9
9.6 approx.	123.2
Mean	123.5

Guye & Fréedericksz [18] determined the rigidity of vitreous silica at 4 temperatures between 57° and —194°C, by measurements of the period of torsional oscillation of a loaded silica fiber having an average diameter of 0.612 mm. The results are:

Temp. °C	R
56.6	225.9
0	225.5
— 80.3	223.3
—194	220.1

The direction and relative magnitude of the change in rigidity with temperature can be found from the change in the period of torsional oscillation of a fiber even though exact measurements of the radius of the fiber are lacking. The equation for the period: $P = 2\pi\sqrt{\frac{I}{M}}$, (in which I = moment of inertia and M = moment of the torsional couple produced in the twisted fiber, M being proportional to the rigidity R) shows that the period changes in the opposite direction to the rigidity.

Part of Horton's measurements, as well as those of Threlfall, of Barnett, of Guye & Einhorn, and of Guye & Morein, are relative measurements of the kind just referred to.

Horton's measurements at temperatures above 100° were made on 3 fibers, made from different specimens of quartz. Their diameter was about 60 μ and their length 100 mm. They were heated in a narrow platinum tube, with water-cooled ends, carrying an electric current. The period was determined at intervals of about 50° from room temperature up to about 1060°C. The rigidity at each temperature was calculated from the ratio of the period to that at room temperature, the rigidity at room temperature being taken as 300.1, the mean of the set of measurements already described (Tab. XXIII.4).

The results are given in Table XXIII.8 and plotted in Figure XXIII.3. (The data on logarithmic decrement will be considered in the latter part of the chapter.)

Barnett's experiments [19] show the general character of the change in rigidity between 0 and 100°. Barnett compared the oscillation periods of a fiber about 20 μ in diameter at 10 temperatures between 18 and 96°, and found that the period decreased proportionally to the increase of temperature.

Measurements on 7 fibers at room temperature and at about 98° then

[18] Article cited.
[19] Article cited in note [8].

served to determine the average temperature-coefficient of rigidity. The results are given in Table XXIII.9.

TABLE XXIII.8.

CHANGE IN RIGIDITY AND LOGARITHMIC DECREMENT OF VITREOUS SILICA FIBERS WITH TEMPERATURE. HORTON, 1905.

Temp. °C	Rigidity Kilomegabaryes	Observed decrement $10^3 L$	Decrement due to fiber alone
20.52	300.17	1.789	0.044
170	304.48	1.812	0.067
296	308.05	1.823	0.078
404	310.59	1.913	0.168
483	312.19	2.008	0.263
613	315.04	2.440	0.695
656	315.75	2.846	1.101
673	316.10	....	....
700	316.60	4.043	2.298
766	317.44	7.781	6.036
795	317.75	10.41	8.67
833	317.75	14.43	12.69
876	317.99	19.67	17.93
919	317.98	24.47	22.73
948	317.57	30.09	28.35
988	315.60	41.65	39.91
1005	313.91	75.47	73.73
1008	307.78	166.2	164.5
1008	305.23	....	....
1058	<283.	335.	333.
22.10	298.47	1.762	0.017

TABLE XXIII.9.

DATA ON THE TEMPERATURE COEFFICIENT OF RIGIDITY OF VITREOUS SILICA FIBERS. BARNETT, 1898.

Temperatures, °C		Approximate diameter of fiber mm	Coefficient of increase of rigidity per degree, $\times 10^6$
Lower	Upper		
20.3	97.2	....	114
17.9	96.7	0.07	123
17.8	96.9	0.04	115
19.2	98.1	0.06	102
17.6	98.2	0.06	119
18.3	96.9	....	117
17.8	96.0	0.02	115
		Mean	115

Threlfall[20] made similar measurements to find the temperature coefficient. He determined the torsional rigidity of a fiber at 22° and 98.5°, from which the mean change of rigidity per degree is calculated to be $+132 \times 10^{-6}$. (This is recalculated from the published data, using the value 0.5×10^{-6} for

[20] Article cited in note [7].

the linear expansion-coefficient of vitreous silica, which Threlfall was not able to determine satisfactorily).

The experiments of Guye and collaborators consist of determinations of the period and logarithmic decrement (see p. 452) of vitreous silica fibers of various sizes and at various temperatures. Four series are of interest in connection with the change of rigidity with temperature, namely, (1) Guye & Fréedericksz, (2) Guye & Einhorn, (3) Guye & Morein, (4) Pazziani & Guye.

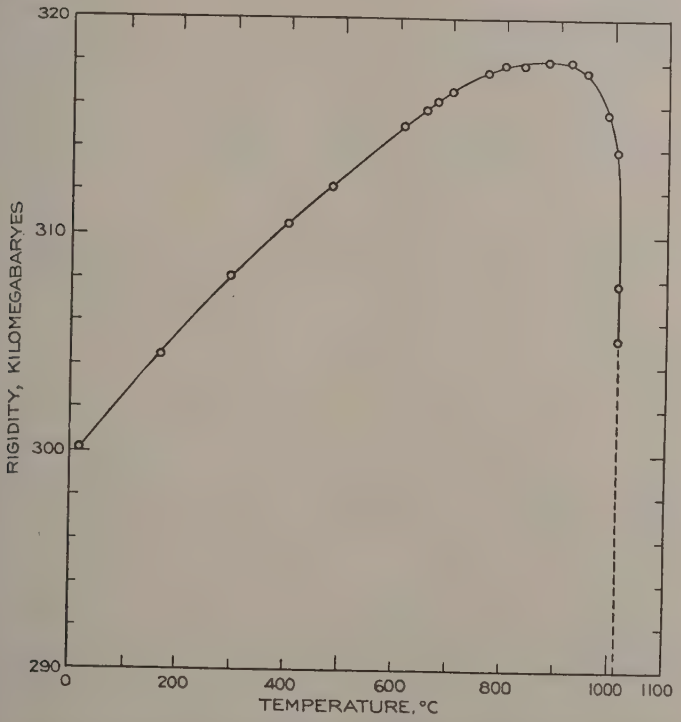


FIG. XXIII.3.—Change of rigidity of vitreous silica fiber with temperature. Data of Horton, 1905.

The first of these has already been noticed (p. 440).

Guye & Einhorn [21] made measurements at 5 temperatures between that of the room and that of liquid air.

Guye & Morein [22] used a slightly different method, in that the fiber did not carry the oscillating load directly but was fastened to the under side of the

[21] GUYE, C. E., & EINHORN-BODZECHOWSKI, M., Arch. sci. phys. nat. (1916) (4) **41**: 287-311, 376-400, 457-468.

[22] GUYE, C. E., & MOREIN, A., Arch. sci. phys. nat. (1920) (5) **2**: 351-371.

load, which was suspended by a steel wire, the wire and the fiber acting jointly to control the oscillations of the load.

The measurements of Guye & Morein were made at 6 temperatures between that of the room and 325°C. Each fiber was held at 325° for several hours, and observations were then made at successively lower temperatures down to 20°, after which the series was repeated from 20° up to 325°. The two series agreed within the limit of error caused by the temperature measurements. These, however, were relatively inexact, because the temperature was estimated from the value of the heating current, after the apparatus had been initially standardized with a thermometer.

The apparatus used by Pazziani & Guye[23] was similar to that of Guye & Morein. The air pressure varied between 10 and 30 mm. Six fibers, of diameters from about 0.2 to 0.5 mm, were employed, and two of them were tested after being annealed at 700 to 800°. The range of the measurements was —20 to 330°. Periods of oscillation were measured photographically, using the stroboscopic method of Lippmann.

TABLE XXIII.10.

EFFECT OF LOW TEMPERATURES ON THE PERIOD OF TORSIONAL OSCILLATION OF VITREOUS SILICA FIBERS. GUYE & EINHORN, 1916.

Diameter of fiber mm	Moment of inertia g/sq. cm	Period, seconds			
		At atmos. temp.	At 0°	At —79°	At —194°
0.51	897	1.791	1.793	1.798	1.811
0.55	897	1.475	1.477	1.484	1.500
0.49	897	1.865	1.866	1.877	1.897
0.48	897	1.905	1.907	1.915	1.930
0.55	3400	2.881	2.885	2.901	2.921
0.49	3400	3.643	3.645	3.666	3.689

The change of rigidity due to cooling below room temperature is shown by Guye & Einhorn's measurements of torsional period to be a *decrease.* This is in agreement with the observations by Horton and others, which show an increase in rigidity when the glass is heated above room temperature. Guye & Einhorn's data on period and temperature for vitreous silica are assembled in Table XXIII.10.

The change of period with temperature in Table XXIII.10 is evidently not linear, and it is not the same for all the fibers. The approximate ratios are:

$$\frac{P \text{ at } -79°}{P \text{ at } 0°} = \text{from } 1.003 \text{ to } 1.006$$

$$\frac{P \text{ at } -194°}{P \text{ at } 0°} = \text{from } 1.010 \text{ to } 1.017$$

[23] PAZZIANI, A., & GUYE, C. E., *Influence du recuit sur le frottement intérieur des fils de quartz aux températures élevées,* Arch. sci. phys. nat. (1924) (5) **6**: 47-64, 89-115, 2 pls.

The rigidity is therefore decreased by 2 to 3½ per cent when the temperature is lowered from 0° to −194°.

Guye & Morein's measurements of torsional period (Table XXIII.11) show that the rigidity continues to increase, above room temperature, until it reaches a maximum, which comes at the same temperature as that at which the logarithmic decrement of the oscillation reaches a minimum. This temperature varies with the diameter of the fiber, and lies between 110 and 210°C for the fibers studied.

This is much lower than Horton's maximum, and its existence is not confirmed by the later measurements of Pazziani & Guye,[24] who observed a continuous increase in rigidity from −20° to 320°.

TABLE XXIII.11.

CHANGE OF RIGIDITY AND LOGARITHMIC DECREMENT OF VITREOUS SILICA WITH TEMPERATURE. GUYE & MOREIN, 1920.

Fiber diameter, 0.620 mm; length, 225 mm. Pressure, 25 mm mercury. Moment of inertia, 1710 c.g.s.

t °C	Period of torsional vibration—Seconds	Logarithmic decrement $1000\,L$
18	6.20	14.04
80	6.16	10.11
150	6.10	9.97
200	6.15	11.32
275	6.18	13.59
325	6.24	18.76

Effect of temperature on Young's modulus

Lees, Andrews & Shave[25] determined the relative change in Young's modulus for vitreous silica up to about 850°, by measuring the bending of rods about 5 cm long, clamped at one end and carrying a weight at the free end, and heated in an electric furnace. Since the rods were not of uniform diameter, the absolute values are not very accurate, and I have therefore recalculated the data in the form of ratios of the modulus at t° to that at 20°. The results are plotted in Figure XXIII.4.

The curves are described in the Figure. The temperature was raised in each instance until viscous flow began to be visible. This occurred at the following temperatures: I, 794°; II, 615°; III, 850°; V, 805°.

The variation in curve IV seems too large to be accidental. It may represent an effect of permanent bending at the close of the previous heating. This would occur near the clamped end. The effect of any element of the rod upon the deflection of the free end is proportional to the cube of the distance from that end, hence the part next the clamp is the most effective, and any internal rearrangement or distortion might be expected to have a marked effect on the next series of measurements, if its position relative to the bar were changed by rotating it, as was done just before curve IV was taken.

Curve VI is for a silica thread, and represents the reciprocal of the

[24] PAZZIANI, A., & GUYE, C. E., p. 114 of article cited.

[25] LEES, C. H., ANDREWS, J. P., & SHAVE, L. S., Proc. Physical Soc. London (1924) **36**: 405-416.

deflection, to which the modulus is proportional; the dimensions are too uncertain to permit direct calculation of the modulus itself.

Change in rigidity with time

Barnett tested the effect of age on the rigidity of vitreous silica fibers. Measurements of the time of oscillation were made over a period of 130 days, with fibers about 20 cm long and from about 28 μ to about 36 μ in diameter. With the exception of small differences which were shown to be due to minor variations of temperature, the periods of oscillation were quite constant.

Horton observed a permanent increase in rigidity in a fiber which had been heated at 33° or higher for several hours while its period of oscillation was being measured. This is shown by the data in Table XXIII.7.

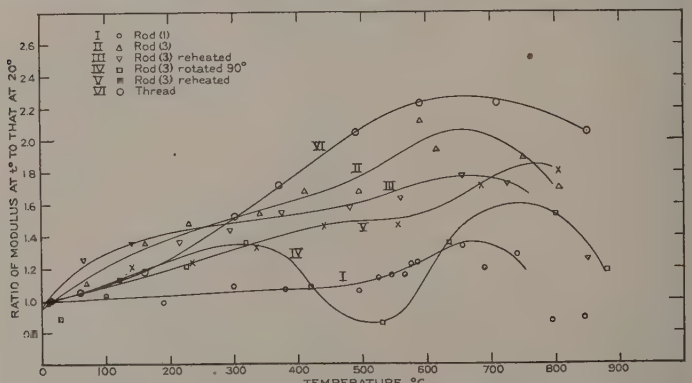

I Rod (1)
II Rod (3)
III Rod (3) reheated
IV Rod (3) rotated 90°
V Rod (3) reheated
VI Thread
RATIO OF MODULUS AT t° TO THAT AT 20°
TEMPERATURE, °C.

FIG. XXIII.4.—Measurements of Lees, Andrews, & Shave on the effect of temperature on Young's modulus for vitreous silica.

In addition to this permanent increase at room temperature there were small but easily measurable changes at all of the various temperatures up to 100°, depending upon the time of maintenance. These changes, as is evident from Table XXIII.7, were sometimes positive and sometimes negative. Even at room temperature the fiber, on being allowed to rest for 3 weeks, increased in rigidity, decreasing again to its normal "annealed" value after being heated to 100°. In comparing the figures in Table XXIII.7 it is to be remembered that the precision is about 0.003 kilomegabarye, and the change per degree is about 0.037 kmb.

The permanent increase in the rigidity at room temperature which followed upon heating the fiber at temperatures below 100° was observed by Horton also in the fibers heated above 100°, provided the maximum temperature did not exceed 760°. The rigidity at room temperature was decreased by heating the fiber to higher temperatures than 760°.

The foregoing observations are in general accord with the qualitative

statement made by Shenstone,[26] that vitreous silica "gains very distinctly in regard to its elasticity" by being heated and then chilled suddenly in water or liquid air. It is evident that some change in constitution or structure takes place at the higher temperature and is then preserved for a long time, perhaps indefinitely, by rapid cooling to the lower temperature.

Imperfect and retarded self-reversing effects of stress

In the preceding portions of this chapter we have considered only the "instantaneous" effects of pressure and stress, by which we mean simply those which occur so promptly that we cannot experimentally measure the time elapsing between the application of the force and the appearance of the deformation.

But there are some substances, among which vitreous silica is included, which show an "elastic after-effect." This arises from three causes, one of which belongs properly in the next chapter, but must be included here because of the practical difficulty of separating the effects quantitatively. They are:

(A) Imperfect elasticity. The deformation under a given stress is greater if the stress is decreasing from a higher value than if it is increasing from a lower value. The effect is analogous to true hysteresis in magnetism, and so is independent of time.

(B) Retarded elasticity. As viewed from opposite sides it may be described thus:

(B1) After the force or load has been applied and the resulting instantaneous deformation has occurred, a further slow deformation takes place which gradually reaches a limit, the load still remaining constant.

(B2) After the load has been removed and the instantaneous restoration has occurred, the body is found to be still slightly deformed and the complete restoration of the original shape takes a measurable time.

(C) Flow. A small but continuous and non-reversing deformation may take place.

This introduction of a time element, particularly in (B), adds a new complication to the elastic phenomena. Especially is this the case in dealing with vibrations, for in order to take a broad and logical view of the matter we must assume that the visibly retarded elastic effects are but the accessible residue of the phenomena taken as a whole, and that all stages of the deformation have a time factor, down to the infinitesimal beginnings of deformation under the infinitesimal beginnings of stress.

The elastic after-effect in torsion is easy to observe. It can be directly seen in a fine fiber of vitreous silica carrying a suspended load, if the fiber be given a sufficiently large twist, but the effect is much smaller than it is in soft glass or in wires of most metals. This is one of the reasons why vitreous silica fibers are preferred as suspensions in physical instruments.

[26] Shenstone, W. A., Proc. Roy. Inst. (1902) 16: 525-531; Nature (1901) 64: 65-67.

Logarithmic decrement of oscillations

While the time element in the elasticity of vitreous silica can thus be observed directly, it is also brought out particularly well in an indirect way, in the torsional oscillations of silica rods or fibers. If a weight is suspended by such a fiber and is given an initial twist, it will oscillate to and fro about the axis of the fiber, but with a gradually decreasing amplitude, even though conditions are carefully controlled so that there is no energy lost by external friction or by transmission to the support. The successive departures from the mean position are found to be in a geometric series, or, in other words, the difference between the logarithms of two successive amplitudes remains constant. This constant quantity is usually called the *logarithmic decrement, L.* It gives a quantitative statement of the effects of imperfect elasticity, retarded elasticity, and possibly flow, on the oscillations of the fiber.

The logarithmic decrement of silica fibers is found to be influenced by the following variables:

For a given fiber, it may be influenced by:

(1) The magnitude of the force, i.e., the *amplitude* of the oscillation;
(2) The speed of application of the force, i.e., the *period* of the oscillation, usually controlled experimentally by changing the moment of inertia of the oscillating weight;
(3) The *temperature;*
(4) The thermal history of the fiber since the last preceding measurement of the decrement;

while for different fibers, the decrement may be influenced by:

(5) The diameter of the fiber.

The effects of amplitude and of period are relatively small. They will be considered more fully in the detailed discussion of the experimental data. The most important variable is the temperature. The logarithmic decrement at liquid-air temperatures is extremely small, so small as to be hardly measurable. It increases gradually with temperature, becoming readily measurable at room temperature. There is some evidence of a passage through a minimum at temperatures between 100 and 300°, but the evidence is not entirely clear. Above 650° the decrement increases rapidly, until at 1000° the oscillation is nearly dead-beat.

Experimental data on elastic after-effect in vitreous silica

Fibers of vitreous silica show directly a torsional elastic after-effect. Threlfall[27] found that it appeared in a fiber 0.102 mm in diameter when the fiber had been twisted one complete turn (360°) per 20 mm of length. C. V. Boys[28] also observed it, noting that it was only about one-fiftieth of that of unannealed soft glass, or one-tenth that of annealed soft glass.

[27] Article cited in note [7].

[28] Boys, C. V., Proc. Physical Soc. Lond. (1887) **9**: 8-19; Phil. Mag. (1887) **23**: 489-499.

Effect of amplitude

The proper measure of the maximum strain produced in a cylindrical rod or fiber by torsion is not the angular twist per unit length but the arc of surface displacement per unit length, or $r\theta/l$. This is the maximum shear strain, the quantity which should be considered in studying the effect of the amplitude of the oscillation.

The after-effect in torsion becomes directly visible only after a twist of about 180 degrees per cm of length of a 0.1 mm fiber, which is a strain of 0.015 in the above-described units.

It might therefore be expected that the effect of amplitude on the logarithmic decrement of the oscillation of 0.5-mm fibers twisted only about 0.2 degree per cm (maximum shear strain $= 87 \times 10^{-6}$) would be inappreciable. Measurements by Guye & Einhorn[29] show that at 18°C the effect is very nearly inappreciable, but not entirely so. The logarithmic decrement does fall off a little as the amplitude decreases, but by an amount which is about on the limit of accuracy of the measurements and is insignificant when compared with the large changes brought about by certain other variables.

Earlier measurements by Guye & Fréedericksz with a 0.6 mm fiber also confirm the existence of a slight decrease in decrement with decreasing amplitude. The maximum strain is not specifically stated but from the general description is evidently not over 121×10^{-6}. The values of the constant b in an empirical formula for logarithmic decrement: $L = L_0 (1 + bA)$, in which L_0 is the decrement (natural logarithm) at infinitesimal amplitude, and A is the amplitude in cm at a distance of 180 cm from the mirror, are:

Temp. °C	$10^3 b$
56.6	0.037
0	0.108
— 80.3	0.320
— 194	0.044

Horton could find no effect of amplitude on the logarithmic decrement of 2 fibers of diameter 0.022 and 0.010 mm, for amplitudes up to 10 degrees, equivalent to a strain of about $(6 \text{ to } 14) \times 10^{-6}$. It should be noted, however, that these oscillations were in air at atmospheric pressure, and that about 97 per cent of the total decrement is due to air friction, so that any small variation due to the silica would be likely to be masked.

Much larger effects than those noted above were observed by Pazziani & Guye.[30] For example, a decrease in the maximum shear strain of fiber No. 6 from 60×10^{-6} to 50×10^{-6} lowered the decrement by 19 per cent, and a similar decrease in the strain of No. 5 from 90×10^{-6} to 41×10^{-6} lowered it by 63 per cent. The question of air damping must again be raised in connection with these results (see p. 457).

Effect of period

In contrast with the usual small effect of varying amplitude, the effect of varying period of oscillation is easily measurable. It is small at room tem-

[29] Article cited in note [21].
[30] Article cited in note [23].

peratures, but becomes relatively large at very low temperatures. This is shown by Table XXIII.12, containing measurements by Guye & Einhorn.

Above room temperatures, up to 325°, the effect of varying period becomes inappreciable, as has been shown by Guye & Morein. They found that the logarithmic decrement of the torsional vibrations of silica fibers is the same (within the limits of error due to the temperature measurement) for moments of inertia of 1710 and 310 c.g.s. units, between 20 and 325°. The periods were 3.03 and 7.13 seconds.

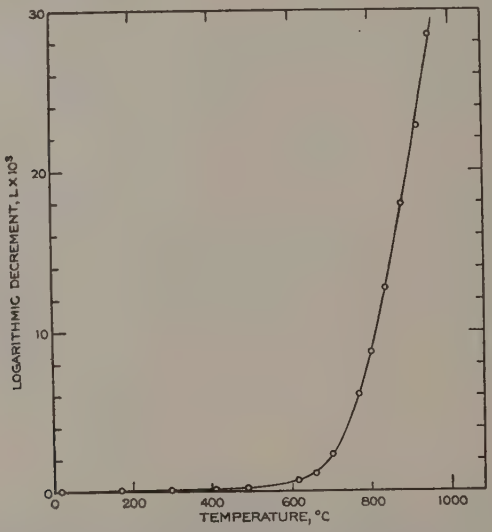


FIG. XXIII.5.—Effect of temperature on the logarithmic decrement of torsional oscillation of a vitreous silica fiber. Horton, 1905.

TABLE XXIII.12.

INFLUENCE OF PERIOD OF OSCILLATION ON THE LOGARITHMIC DECREMENT OF TORSIONAL OSCILLATIONS OF VITREOUS SILICA. GUYE & EINHORN, 1916.

Temperature °C	Diameter of fiber = 0.49 mm				Diameter of fiber = 0.55 mm			
	Faster oscillation		Slower oscillation		Faster oscillation		Slower oscillation	
	Period Sec.	1000 L	Period Sec.	1000 L	Period Sec.	1000 L	Period Sec.	1000 L
21	1.865	3.31	3.643	3.23	1.475 (17°)	2.96	2.881 (19°)	3.08
0	1.866	1.61	3.645	1.56	1.477	1.65	2.885	1.57
— 79	1.877	0.72	3.666	0.62	1.484	0.64	2.901	0.54
— 194	1.897	0.67	3.689	0.57	1.500	0.58	2.921	0.46

Effect of temperature

By far the most important factor in the logarithmic decrement is the temperature. Unfortunately the experimental data are still too incomplete and in some respects too inconsistent to permit of any general statement as to the effects of temperature alone. The confusion is caused by the incompletely known effects of the final two variables mentioned at p. 452, namely, the previous thermal history of the fiber, and the diameter of the fiber. The best that can be done at the moment is to present the experimental data in the form of a set of curves, which is done in Figures XXIII.5, 6, and 7. Figure XXIII.5 contains the results of Horton. Figure XXIII.6 includes two sets of determinations: those of Guye & Einhorn, and those of Guye & Morein. Figure XXIII.7 contains the data of Pazziani & Guye.

Horton's measurements.—In connection with his experiments on the change of rigidity with temperature, Horton also measured the logarithmic decrement of his silica fibers. His apparatus was not evacuated, and the greater part of the decrement at room temperatures was therefore due to air friction. The proportion was measured by timing oscillations on the same fiber both in air and in hydrogen, with the result that 3.27, 2.44, and 2.49 per cent of the total decrement was found to be due to the 3 fibers of diameters 12.7, 16.9, and 22.4 μ, respectively, the rest being due to air. This general proportion was confirmed by further experiments with heavier fibers, which yielded proportions varying from 0 to 5 per cent, this variation being due largely to the very small magnitude of the decrement in the larger fibers. It was therefore assumed in the subsequent high-temperature experiments that 97.5 per cent of the decrement observed at room temperature was due to air friction, and that the damping thus estimated was the same in absolute amount at all temperatures because it is due almost entirely to the vibrator, which remains cold. This kind of a calculation makes the values of L calculated at temperatures up to about 500° relatively inaccurate, but the probability of error rapidly diminishes at higher temperatures. The results are included in Table XXIII.8, and are plotted in Figure XXIII.5.

TABLE XXIII.13.

ESTIMATED LOGARITHMIC DECREMENT OF VITREOUS SILICA FIBER BETWEEN ROOM TEMPERATURE AND 100°. HORTON, 1905.

Temperature, °C	Observed decrement $10^3 L$	Decrement due to air $10^3 L$	Decrement due to fiber $10^3 L$
15.25	12.48	12.04	0.44
33.27	13.05	12.61	0.44
54.89	13.84	13.29	0.55
72.64	14.29	13.84	0.45
97.40	15.14	14.61	0.53

Horton made a similar estimate of the logarithmic decrement due to the fiber alone from his experiments between room temperature and 100° (p. 444). In this case the vibrator, as well as the fiber, was heated. Correction must therefore be made for the increased viscosity of the air, and this was done

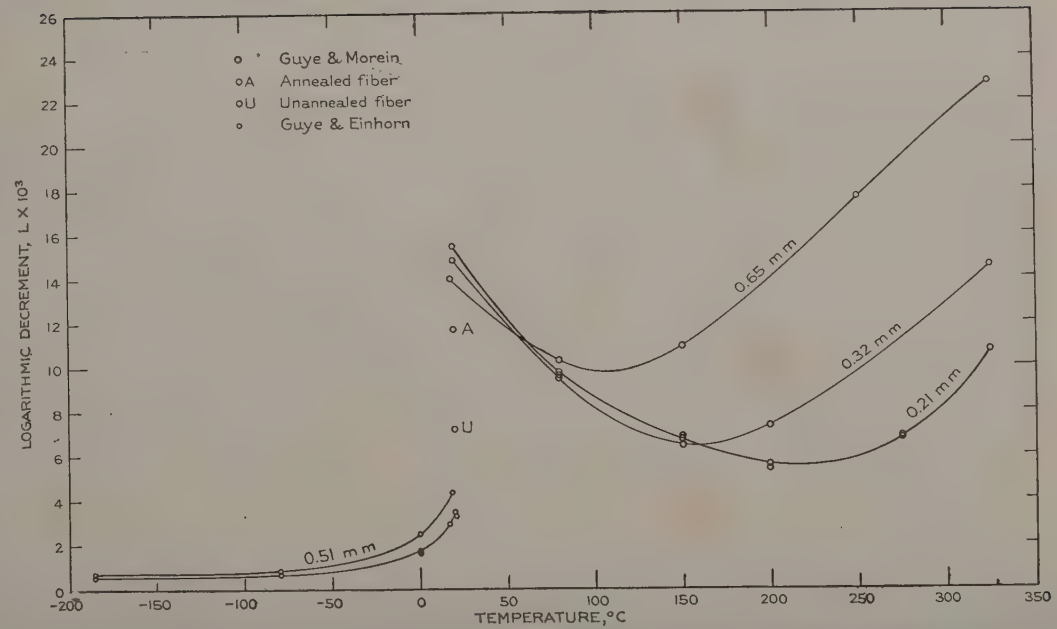


FIG. XXIII.6.—Effect of temperature on the logarithmic decrement of torsional oscillation of a vitreous silica fiber. Data of Guye & Einhorn and of Guye & Morein.

on the basis of Holman's data (1886). The results are given in Table XXIII.13, and indicate that the logarithmic decrement does not change greatly between room temperature and 100°.

Guye and collaborators.—The measurements of Guye & Einhorn and of Guye & Morein, plotted in Figure XXIII.6, and given in part in Table XXIII.12, were made on much larger fibers than Horton's, and in an apparatus which could be evacuated to avoid the disturbances due to air friction. The first of these two sets covers the range from liquid air to room temperature; the second, from room temperature to 325°. For these two ranges the measurements should have higher precision than those of Horton.

What is lacking now is a series to connect these two ranges. Since they touch only at room temperature and overlap hardly at all, the only opportunity for disagreement between the two is at that temperature. Unfortunately there is a serious discrepancy just here, for Guye & Morein's unannealed fibers have a much higher decrement than Guye & Einhorn's unannealed fibers of about the same size. Now there is one notable difference between the two sets, namely, that Guye & Einhorn's measurements were made under an air pressure of 1 mm of mercury, while Guye & Morein's were at 25 mm. One can scarcely avoid the inference, in view of Horton's experiments showing that 97.5 per cent of his decrement at room temperature was due to air, that Guye & Morein's data are subject to a large correction which might help to bring them into line with the low-temperature data. This correction, as in Horton's case, would diminish with increasing decrement.

The experimental difficulties in obtaining comparable results are illustrated by the measurements of Pazziani & Guye,[31] whose values for the decrements of 6 silica fibers are shown in Figure XXIII.7. It will be noted that the curve for falling temperature never duplicates that for rising temperature, but usually falls below it. (No. 3 is an exception.) In every case there is a minimum above 100°. This minimum persists in Nos. 1A and 4A, which have been annealed at 700 to 800°.

The values of 10^3L at room temperature are from 6 to 19, and thus fall between the two sets illustrated in Figure XXIII.6. The query already made concerning the possibly large damping effect of air applies here also, although the authors investigated the effect of pressure to the extent of finding that a decrease of pressure from 736 to 10 mm lowered the decrement of No. 5 from 14.24 to 12.79, or 9.6 per cent.

Measurements of the logarithmic decrement of a vitreous silica fiber of average diameter 0.612 mm were also made at an earlier date (1910) by Guye & Fréedericksz,[32] at temperatures of 50, 0, —80, and —194°, but the fiber was irregular and the results are probably not sufficiently reliable for inclusion with the later data already presented. They confirm the fact that the logarithmic decrement at low temperatures is very small.

With respect to the low-temperature measurements by Guye & Fréedericksz and by Guye & Einhorn the question was specifically raised whether the very small decrements found might not be due partly to air friction, even though the air pressure was small, or to transmission of energy to

[31] Article cited in note [28].
[32] Article cited in note [9].

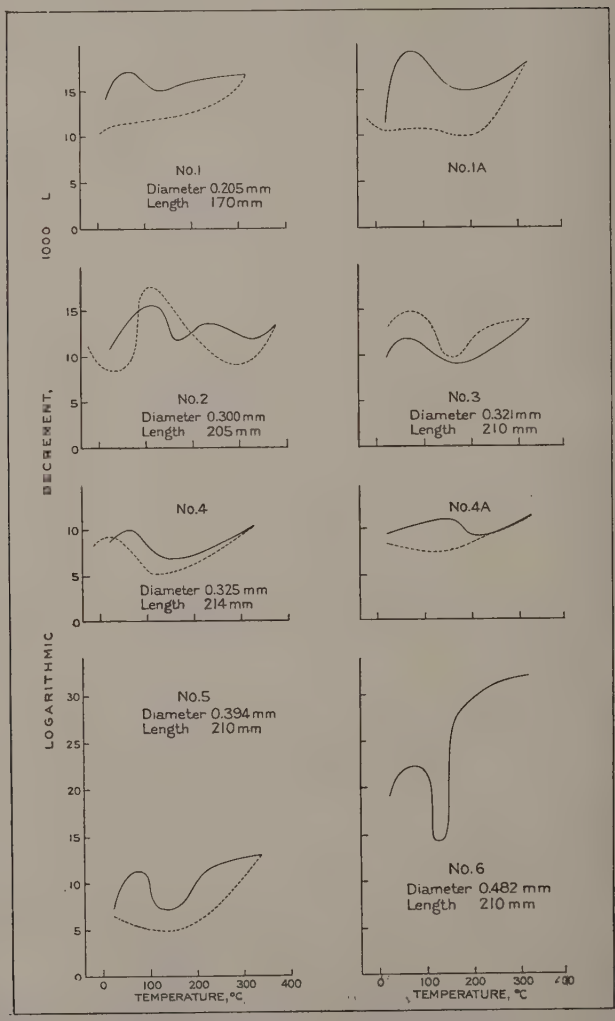


FIG. XXIII.7.—Pazziani & Guye's experiments on the effect of temperature upon the logarithmic decrement of vitreous silica fibers.

the support. Guye & Barbier [33] brought evidence to show that air friction is not the cause; the decrement in carbon dioxide at a pressure of 1 cm of mercury was found by them to be the same, within 1 per cent, as in air at similar pressure while there should have been a change of 17 per cent if the gas were alone responsible.

Effect of previous thermal history

Regarding the effect of previous thermal history of the glass, the following general statements may be made on the basis of the two sets of data exhibited in Figure XXIII.6:

(A) If a fresh fiber is cooled to —194° it undergoes some change of structure which makes its logarithmic decrement permanently higher than before, for the range of temperature 20 to —194°.

(B) If a fresh fiber is heated to 325° it undergoes some change of structure which makes its logarithmic decrement permanently higher than before, for the range 20 to 325°; and the change is relatively much greater than that due to cooling to —194°.

The large effect of the "annealing" by heating to 325 to 350° is shown in Table XXIII.14.

TABLE XXIII.14.

EFFECT OF ANNEALING ON THE LOGARITHMIC DECREMENT OF TORSIONAL OSCILLATIONS OF VITREOUS SILICA AT ROOM TEMPERATURES.

(Values of $10^3 L$)

Diameter of fiber	As drawn, before annealing	After annealing
0.580 mm	9.37 9.41 } 9.43 9.50	13.53 13.37 } 13.52 (325°) 13.65
0.690 mm	7.20	11.70 (350°)

The experiments of Pazziani & Guye were specifically directed toward finding the effect of annealing upon the logarithmic decrement. In Figure XXIII.7, No. 1A is the curve of fiber No. 1 after it had been heated for 12 hours at 800°. No. 4A is for No. 4 after heating for 15 hours at 700°. No definite conclusion as to the effect of this annealing can be drawn from the curves.

For fibers of a Jena alumina-potash glass the temperature-decrement curve was rendered reversible by annealing at 600°. No such reversibility was attained by the annealing of silica.

From experience with thermal dilatation and other properties it appears likely that annealing above 1050° will be necessary in order to secure complete reproducibility.

Effect of diameter

Regarding the effect of diameter of fiber the following general statements may be made on the basis of the two sets of data presented in Figure XXIII.6:

[33] GUYE, C. E., & BARBIER, P., Arch. sci. phys. nat. (1918) (4) **46**: 326-328.

(A) The logarithmic decrement at the higher temperatures is much greater for large fibers than for small fibers.

(B) At room temperatures the relation is reversed, and the logarithmic decrement is greater for the small fibers, as may be seen from Table XXIII.15; but the difference is not large.

(C) The minimum of decrement comes at a lower temperature, the larger the fiber.

TABLE XXIII.15.

VARIATION OF THE LOGARITHMIC DECREMENT OF TORSIONAL OSCILLATIONS OF ANNEALED VITREOUS SILICA AT ROOM TEMPERATURES, WITH DIAMETER OF FIBER. GUYE & MOREIN.

Diameter of fiber mm	t	$10^3 L$
0.208	20°	15.42 *
		15.79 **
0.320	20°	14.78 *
		14.96 **
0.620	18°	14.04 *
0.654	18°	13.95
		13.63 †

* Load with large moment of inertia.
** Load with small moment of inertia.
† Measured at different amplitude.

The measurements of Pazziani & Guye (Figure XXIII.7) are so much more irregular than those represented in Figure XXIII.6 that the above generalizations can be neither supported nor refuted. The largest fiber (No. 6) has a considerably greater decrement, both when hot and when cold, than any of the others, and to this extent agrees with principle (A), but the other five show no systematic relation.

As for principle (C), the minima of the curves of Figure XXIII.7 all fall between the limits 120 and 210°.

The diameter of the fiber had a large effect in Horton's experiments, as shown by the following data:

Diameter μ	Length mm	Period Sec.	Decrement in air $10^3 L$	Decrement in hydrogen $10^3 L$	Decrement due to fiber $10^3 L$
12.76	114.5	23.30	33.92	17.14	1.11
16.92	114.5	13.27	19.64	9.84	0.48
22.4	74.0	6.00	9.66	4.84	0.24

THEORY OF ELASTIC AFTER-EFFECT AND THE OSCILLATIONS OF VITREOUS SILICA FIBERS

The theory of damped oscillations has interested physicists for 150 years, beginning with Coulomb's attempted solution in 1784. Out of the discussions and experiments that have followed, especially as applied to

the oscillations of a twisted fiber, there have emerged two contrasted theories.

The one, most completely presented by Boltzmann, assumes that the resistance to deformation in imperfect and retarded elasticity is of the character of an "elastic reactivity." It depends upon all the deformations which the body has undergone previous to the moment considered, their effect being the less, the longer the time which has elapsed since they took place. A logical deduction from this theory is that the logarithmic decrement should be *independent* of the period of oscillation.

The other theory, worked out by Voigt, ascribes the resistance against deformation to a true friction, proportional to the speed, and exactly analogous to the viscosity of a liquid. The logical consequence of this theory is that the logarithmic decrement should be *inversely proportional* to the period of the oscillation.

Experiments show that most substances do not fit exactly either of these theories, but fall somewhere between. Vitreous silica, however, at temperatures of about 100 to 350°, agrees very well with the Boltzmann theory; its resistance to deformation is a function of all the deformations which it has already undergone, but is not dependent on the momentary speed of application of the force. But as the temperature falls, vitreous silica begins to depart from the ideal Boltzmann condition, and the deformation begins to be dependent on the rate of the application of the force, though it never reaches complete agreement with the Voigt theory even at the lowest temperature studied (— 194°).

The atomic mechanism of the elastic retardation may be pictured as follows. At the higher temperatures the atoms quickly reach a condition of equilibrium at each step in the deformation. Their configuration at any moment, resulting from preceding deformations, is the principal factor in deciding the resistance to the next step in the application of the force. At low temperatures, on the other hand, equilibrium is attained at a rate which is slow compared to the rate of application of the force. Although the momentary configuration is still the most important factor, there is added the condition that the effects of the applied force are transmitted but slowly across successive sheets of the material moving in the direction of flow, a condition which is equivalent to viscosity in a liquid, and which tends to make the deformation depend upon the speed of application of the force at the instant.

As for the influence of temperature on the elastic retardation, both the evidence and the theory are in a very unsatisfactory state. The data contain several contradictions.

Guye & Morein state their belief that "sufficiently energetic and prolonged annealing" would bring the silica fibers to a uniform state in which all would show the same logarithmic decrement.

The existing data seem to indicate rather the contrary. The large effect of heating to 325° seen in Table XXIII.11 occurred quickly, and the long-

continued heating at 325° and lower temperatures during which the measurements on the variation of decrement with temperature were carried out did not cause any further measurable change. In spite of this cessation of change the larger fibers still show logarithmic decrements which are more than twice as great as those of the smaller fibers.

The matter might be tested by first determining at what temperature the annealing goes on at a controllable rate. Successive annealings at this temperature, followed by measurements of L at room temperature, would show whether L was approaching a value common to all the sizes of fibers, or whether it was approaching asymptotically a specific value for each diameter. According to the general theory which I have set forth in Chapter XV, and the special hypotheses in the same chapter concerning vitreous silica, the second of the above two possibilities is the more likely, and it is to be expected that each fiber will have its own specific limiting value of L.

Furthermore, as already noted at p. 459, it seems unlikely that complete reversibility will be attained by annealing at any temperature below about 1050°.

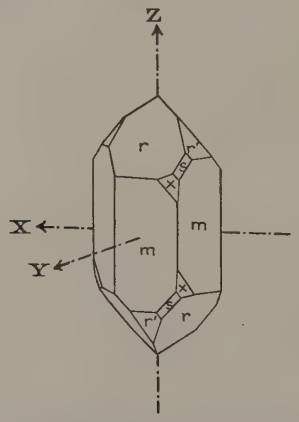


Fig. XXIII.8.—Conventional placing of rectangular coordinate axes for the purpose of stating the elastic constants of low-quartz.

The elastic properties of quartz

The complete statement of the elastic properties of low-quartz at a given temperature can be made in terms of 6 constants (see p. 435).

Before these constants can be given definite numerical magnitudes it is necessary to adopt some orientation of coordinate axes in relation to the elements of symmetry of the crystal. The accepted convention is that of Voigt, illustrated in Figure XXIII.8. The Z-axis coincides with the principal axis of the substance; the Y-axis comes forward through the front face of the positive rhombohedron, the YZ plane being perpen-

dicular to this face; the X-axis is thereby fixed in position, its positive direction being taken to the left.

The six elastic constants

The 6 "principal elastic coefficients" (or Elastizitätsmoduln of Voigt) are given in Table XXIII.16. The unit of stress is the kilomegabarye (see Table XXII.1). The Table also contains the corresponding values of the so-called "principal elastic moduli" (Elastizitätskonstanten). This is not an independent set of constants, because they can be calculated directly from the principal elastic coefficients, or vice versa.

Table XXIII.16.

"Principal Elastic Constants" of Low-Quartz at Room Temperature.

Unit of Stress is the Kilomegabarye (10^9 dyne per sq. cm).

Principal elastic coefficients		Principal elastic moduli	
s_{11}	$1\ 298 \times 10^{-6}$	c_{11}	851
s_{33}	990×10^{-6}	c_{33}	1 053
s_{44}	$2\ 005 \times 10^{-6}$	c_{44}	571
s_{12}	-166×10^{-6}	c_{12}	69.5
s_{13}	-152×10^{-6}	c_{13}	141
s_{14}	-431×10^{-6}	c_{14}	168

Secondary constants

Various useful secondary constants can be calculated from the 6 principal constants.

The coefficient of compressibility (see XXII) is

$$\beta'' = 2(s_{11} + s_{12} + 2s_{13}) + s_{33}$$

The two principal linear compressibilities, the axial and equatorial (see p. 428), are:

$$\gamma_{\parallel} = 2s_{13} + s_{33} \qquad \gamma_{\perp} = s_{11} + s_{12} + s_{13}$$

Young's modulus (see p. 436) changes with the direction, except in the equatorial plane, perpendicular to the principal axis. In this plane it is independent of the direction. Its axial and equatorial values are:

$$E_{\parallel} = \frac{1}{s_{33}} \qquad E_{\perp} = \frac{1}{s_{11}}$$

The value of E in any other direction, defined by its angles θ_1, θ_2, and θ_3 with the coordinate axes, X, Y, and Z, respectively, may be found from the formula:

$$\frac{1}{E} = s_{11}(1 - \cos^2\theta_3)^2 + (s_{44} + 2s_{13})\cos^2\theta_3(1 - \cos^2\theta_3) + s_{33}\cos^4\theta_3 + 2s_{14}\cos\theta_2\cos\theta_3(3\cos^2\theta_1 - \cos^2\theta_2)$$

The secondary constants derived from the six coefficients in Table XXIII.16, using the kilomegabarye as unit of pressure, are:

Coefficient of volume compressibility, $\beta'' = 2646 \times 10^{-6}$
Axial linear compressibility, $\gamma = 686 \times 10^{-6}$
Equatorial linear compressibility, $\gamma_{\perp} = 980 \times 10^{-6}$
Young's modulus, axial, $E_{\parallel} = 1010$
Young's modulus, equatorial, $E_{\perp} = 770$

$$\frac{1}{E} = 1298(1 - \cos^2\theta_3)^2 + 1701\cos^2\theta_3(1 - \cos^2\theta_3) + 990\cos^4\theta_3 - 862\cos\theta_2\cos\theta_3(3\cos^2\theta_1 - \cos^2\theta_2)$$

The experimental data

The only complete set of determinations of the six elastic constants of low-quartz is that of Voigt,[35] and his values are used in Table XXIII.16. He made measurements on the bending and torsion of 27 plates, cut at various orientations from several crystals of left-quartz from Brazil.

In connection with their study of the change of elasticity with temperature, Perrier & Mandrot[36] made numerous measurements of s_{11} and s_{33} at room temperature. Their average results are shown in Table XXIII.17 compared with values derived from Table XXIII.16. The agreement is seen to be fairly close.

Table XXIII.17.

Data on the Elastic Constants of Quartz at Room Temperatures. Perrier & Mandrot, 1923.

Unit of Pressure, Kilomegabarye (10^9 dyne per sq. cm).

Direction			Number of determinations	Temp. °C	Voigt
	$E_{\parallel}$	$10^6 s_{33}$			
$\parallel$ to axis	1028.3	972.5	15	15	$10^6 s_{33} = 990$
$\parallel$ to axis	1029.2	971.6	14	16	
	$E_{\perp}$	$10^6 s_{11}$			
$\perp$ to axis	785.9	1272.4	20	15	$10^6 s_{11} = 1298$
	E_{50}				
At $+50°$ to axis, in plane $\parallel$ to binary axis	769.1		7	15	$E_{50} = 783$
	E_{-50}				
At $-50°$ to axis, in plane $\parallel$ to binary axis	1280.8		4	15	$E_{-50} = 1283$

The value of Young's modulus for quartz in the direction $\perp$ to the threefold and twofold axes can be measured with good precision by means of Cady's application of electromechanical resonance utilizing the piezo-electric property of quartz (see XXVIII). No determinations made by this method have been published, though some have been made on quartz at vibration-frequencies of 100,000 to 2,000,000 per second.[37]

[35] Voigt, W., *Bestimmung der Elasticitätsconstanten von Beryll und Bergkrystall*, Nachr. K. Ges. Wiss. Göttingen **1886**: 93-120, 289-339. Ann. Physik u. Chem. (1887) **31**: 474-501, 701-724.

[36] Article cited below.

[37] Cady, W. G., Physical Rev. (1922) (2) **20**: 98-99.

Linear compressibilities

The linear compressibilities calculated from the constants of Table XXIII.16 may now be compared with Bridgman's experimentally measured values (see p. 429). If p is in kilomegabaryes:

	Bridgman, observed (20°)	Voigt, calculated
$10^6\gamma_{\parallel}$ =	751	686
$10^6\gamma_{\perp}$ =	1071	980
Ratio $\gamma_{\parallel}/\gamma_{\perp}$ =	0.701	0.700

Bridgman's values are both 9 per cent high, but the ratios of the two constants agree remarkably well.

Modulus of penetration

Auerbach obtained the following experimental values for his modulus of penetration (see p. 437) on quartz:

Force $\parallel$ to axis [38]	1042 kilomegabaryes
Force $\perp$ to axis [39]	840 kilomegabaryes

Influence of temperature on the elastic constants of quartz

The influence of temperature on the vibration-frequency of a bar or plate of quartz or vitreous silica is due almost entirely to the change in elastic constants with temperature. As in most vibrating systems, such as tuning forks, the change of dimensions and change of density due to thermal dilatation and deformation (XX) are of small effect compared with the change of elasticity.

Precise quantitative data at room temperatures are lacking, but the general character of the changes in compressibility and in Young's modulus for quartz are known. The compressibility increases a little with temperature (see XXII).

Young's modulus parallel and perpendicular to the axis changes very little near room temperature, but undergoes remarkable changes near the high-low inversion-point, 573°. When quartz is heated above room temperature the modulus decreases, at first slowly, then at a more and more rapid rate, until just before the inversion it is about half as large as at room temperature. Immediately after the inversion it rises to high values again.

The modulus perpendicular to the axis changes much more than does the modulus parallel to the axis. It becomes the larger of the two above the inversion-point, while at atmospheric temperatures the parallel modulus is the larger.

[38] Auerbach, F., Ann. Phys. u. Chem. (1896) **58**: 381-390.
[39] Auerbach, F., Ann. Physik (1900) (4) **3**: 116-119.

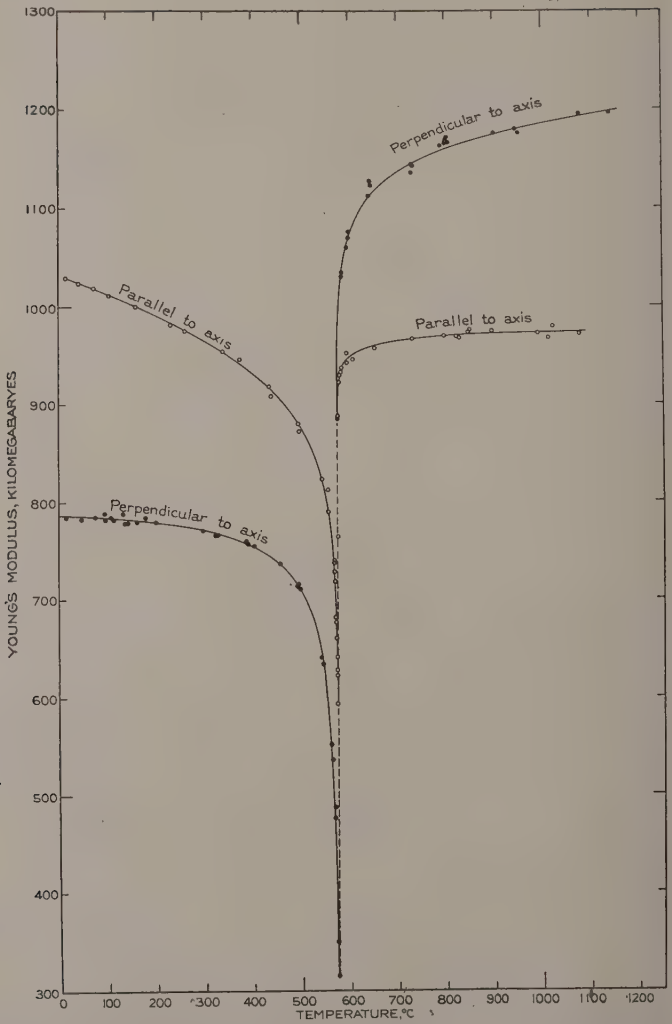


FIG. XXIII.9.—Experimental data on the variation of Young's modulus of quartz with temperature. Perrier & Mandrot, 1923.

To describe these changes in another way, suppose two equal weights suspended by two rods of quartz, one cut parallel and the other perpendicular to the axis. As the temperature rises the elastic stretch produced by the weights increases, the perpendicular-cut rod stretching more than the other, and the stretch increasing rapidly near the inversion. Upon inverting, both rods draw up their weights, the perpendicular-cut rod shrinking much more than the parallel.

It is worthy of note that the rate of change of the elasticity is very small at atmospheric temperatures and again at temperatures several hundred degrees above the inversion-point.

Experimental data

Our knowledge of the effect of temperature on the elasticity of quartz comes almost entirely from the work of Perrier & Mandrot.[40] They cut optically plane-parallel plates of quartz $0.7 \times 7 \times 70$ to 80 mm so as to obtain Young's modulus parallel to the principal (ternary) axis, and also parallel to a twofold (equatorial) axis, perpendicular to the principal axis. A plate was supported near the ends, and the amount of bending produced by a force at the middle point was determined with an optical lever arrangement. The precision was within 0.3 per cent. Measurements were also made on directions perpendicular to a twofold axis but at $+50°$ or $-50°$ to the principal axis.

The phenomena were found to be perfectly reversible, both mechanically and thermally. An apparent irreversibility near the inversion-point is ascribed to the difference between isothermal and adiabatic moduli when the moduli are small, that is, when the extension is large. The absorption of heat on stretching and release of heat on contraction are great enough to have an observable effect on the measurements, unless time enough is allowed for the temperature to become equalized. A period of one or two minutes is usually sufficient.

The data on the isothermal moduli are presented in Figure XXIII.9.

It is of interest to note that the thermal dilatation and the thermal change of elasticity of quartz are related both above and below the inversion-point. Leaving out of account the sudden changes in dimensions and elasticity at the inversion itself, the relation is expressed qualitatively in the statement that the more widely the atoms become separated, the greater the deformation due to a given mechanical force.[41]

Historical notes

Nearly 100 years ago Savart recognized that the elastic properties of quartz are those of a substance of rhombohedral symmetry. This symmetry appeared in his "sound-figures."

[40] Perrier, A., & Mandrot, R. de, *Elasticité et symétrie du quartz aux températures élevées,* Mem. Soc. Vaudoise Sci. Nat. (1923) 1: 333-364. Prelim. publ. in Compt. rend. Acad. Sci. Paris (1922) **175**: 622-624, 1006.

[41] Perrier & Mandrot, article cited.

A sound-figure is produced in a disk or plate when it is set in vibration at some point, usually along the edge. Savart cut three series of quartz plates: one series parallel to the principal axis but oriented at various angles to a binary axis; a second series parallel to a binary axis (axis of twofold symmetry); and a third series parallel to an intermediate axis. (See p. 188.) A plate of an isotropic substance vibrates in four sectors divided by diameters which are perpendicular to each other and symmetrical with respect to the point which is set in vibration. In the quartz plates these diameters were found to be replaced by sound-figures which are hyperbolas; furthermore, the position of the hyperbolas on the plate is fixed and not dependent on the point at which the plate is set into vibration.

Very little more was learned about the elasticity of quartz until Voigt made his careful and thorough measurements in 1886, and not much seems likely to be added to the fundamental constants then established for room temperatures. More recent progress has been in the direction of new measurements of compressibility, and the extension of elasticity measurements to higher temperatures.

Elasticity of the micro-forms

No attempt has been made to correlate elastic properties with direction of the fibers in the micro-fibrous varieties such as chalcedonic silica. The only material examined has been flint and agate, and these have been treated as if elastically isotropic, as in effect they are when studied in specimens of the usual size. Drude & Voigt showed this to be true by comparing the rigidity of two plates, one of which had its broad dimension $\perp$ to the broad dimension of the other. Any aeolotropy would have caused a difference in R, but no difference was observed.

Mallock[42] measured Young's modulus E on agate. Drude & Voigt[43] measured both E and R on translucent gray flint from Rügen. The average results, in kilomegabaryes, are:

	E	R
Mallock	626	—
Drude & Voigt	745	345

Relation of elasticity to the structure of vitreous silica and the micro-forms

By a comparison of elastic constants it is possible to obtain some light on the constitution and structure of vitreous silica and the micro-forms of silica.

Poisson's original theory of elasticity assumed the existence of molecules which exert upon neighboring molecules forces which are the same in all directions, varying only with the distance. On this basis he showed that the ratio of the constants c_{11}/c_{12} of an isotropic substance should be

[42] Mallock, A., Proc. Roy. Soc. Lond. (1891) **49**: 380-398.

[43] Drude, P., & Voigt, W., Ann. Phys. u. Chem. (1891) **42**: 537-548; correction, same, **44**: 168-170.

equal to 3, or, in other words, the value of Poisson's ratio σ should be $\frac{1}{4}$ (see Table XXIII.1). The same holds true even if the atoms and molecules are assumed to exert directed forces, provided only that atomic and molecular groups of a size comparable to that of the atoms are in turn oriented in all possible directions. Experiment, however, shows that for many isotropic substances the value of σ departs more or less widely from $\frac{1}{4}$.

Voigt [44] clarified this situation considerably by developing the theory for a substance which is "quasi-isotropic." While the theory is now rather out of date, it is presented here because it does bring out some interesting facts regarding vitreous and chalcedonic silica.

A quasi-isotropic substance is one which is made up of crystalline particles which are very small in comparison with distances accessible to mechanical experiments, but which are nevertheless large relative to atomic sizes; further, these crystalline particles are oriented in all possible directions, without appreciable gaps between them, and each particle possesses the symmetry and elastic constants of the crystalline substance. Such a quasi-isotropic substance built up of particles whose molecules had no polarity would have its two elastic constants c and c_1 (corresponding to c_{11} and c_{12}) in the ratio 3 as before, but if it were made of particles whose molecules possessed polarity, as exhibited in the crystal symmetry, the ratio would depart from the value 3.

The actual values of the two elastic constants of a quasi-isotropic substance, in terms of the elastic constants of the crystalline substance of which it is built, are given by the equations:

$$c = \frac{1}{5}(3A + 2B + 4C)$$

$$c_1 = \frac{1}{5}(A + 4B - 2C)$$

in which

$$A = \frac{1}{3}(c_{11} + c_{22} + c_{33})$$

$$B = \frac{1}{3}(c_{23} + c_{31} + c_{12})$$

$$C = \frac{1}{3}(c_{44} + c_{55} + c_{66})$$

For low-quartz, the equations reduce to:

$$5c = \frac{4}{3}(2c_{11} + c_{13} + 2c_{44}) + c_{33}$$

$$5c_1 = \frac{1}{3}(c_{11} + 5c_{12} + 8c_{13} + c_{33} - 4c_{44})$$

from which it results that a quasi-isotropic substance made up of particles of quartz would have a ratio c/c_1 equal to 13.7 instead of 3.

[44] Voigt, W., Lehrb. d. Kristallphysik (1910, Leipzig) pp. 954-964.

A detailed comparison of the calculated constants with those determined by Stumpf [45] for vitreous silica is given in Table XXIII.18.

TABLE XXIII.18.

COMPARISON OF THE CALCULATED ELASTIC CONSTANTS OF A QUASI-ISOTROPIC SUBSTANCE MADE UP OF QUARTZ UNITS, AND THE MEASURED CONSTANTS OF VITREOUS SILICA. STUMPF, 1913, RECALCULATED.

Unit of pressure is the kilomegabarye.

Constant	Calculated	Measured
E	1001.	698.8
R	467.	308.5
σ	0.068	0.133
c	1007.	728.2
c_1	73.2	111.2
c/c_1	13.7	6.55

The ratio c/c_1 for vitreous silica is seen to be about 6, midway between the theoretical values 13.7 and 3. The glass would seem, therefore, to be neither isotropic according to the Poisson model, nor an aggregate of submicroscopic but atomically large units having the properties of quartz.

Two explanations may be offered for the value of c/c_1 found for vitreous silica.

In the first place, it may be supposed that the units composing the glass, considered still as a quasi-isotropic substance, are so small as to approach atomic sizes. The theoretical calculation would then no longer be exact, and the value for c/c_1 would lie somewhere between the value 13.7 associated with genuine quasi-isotropy, and the value 3 associated with Poisson's isotropy. Against this supposition Voigt [46] brings the fact that the difference in densities between quartz and vitreous is too great, for it is hardly to be expected that small quartz units only a few atoms in diameter could be packed together in random orientation to make vitreous silica and still allow the large amount of interspace necessary to reduce the density from 2.65 to 2.20.

To aid in disposing of this latter objection, the silica thread hypothesis presented in Chapter XV may be brought forward. It amounts to supposing that the units of the quasi-isotropic solid are small in two dimensions only, but large in the third dimension. The heterogeneous entanglement of these threads would then permit the formation of a solid of much smaller density than quartz, but with a ratio c/c_1 intermediate between the value characteristic of a genuinely quasi-isotropic but fundamentally crystalline silica, and the lower limiting value 3. Such a substance would not show the usual X-ray evidence of crystallinity, for the units would be too narrow.

However this may turn out, a second explanation, also offered by

[45] Article cited in note [12].
[46] STUMPF, pp. 884-886 of article cited in note [12].

Voigt, is admissible. Assume that the glass is isotropic in the Poisson sense, that is, made up of small atom-groups oriented in all directions. Then it must have a value of 3 for the ratio c/c_1 *unless* the elastic displacements assumed in the theory are not quite exactly those of a perfect elastic solid but possess to a slight extent the character of displacements in a liquid. In a perfect liquid $c_1 = 0$ and therefore $c/c_1 = \infty$. The value $c/c_1 = 6$ is therefore suitable to an isotropic solid which is not quite perfectly elastic ($c/c_1 = 3$) but has a very small degree of liquidity.

Elasticity and structure of micro-crystalline silica

The elastic constants of flint are in agreement with the data on its structure given in Chapter X and also support the hypotheses of its structure given in XVI.

X-ray evidence shows the existence of a quartz structure in flint (see p. 160). A substance made up of very small units of quartz, oriented in all possible directions, would have a ratio of the elastic constants c/c_1 of about 14, while for Poisson's ideal isotropic substance the ratio would be only 3. This ratio for flint is found experimentally to be about 12, confirming the optical evidence that flint is an aggregate and not a homogeneous substance. The value 12 is also consistent with the hypothesis that the units of the aggregate are small units having the properties of quartz.

This value is furthermore not inconsistent with the hypothesis that flint consists of small quartz units cemented together with amorphous silica, since the value for a quartz aggregate is estimated at 14, while that of vitreous silica is known to be about 6.

The properties of a cemented aggregate, however, are not so definitely predictable as those of a quasi-isotropic substance made up of only one kind of units. If the cement is itself finely subdivided or powdery in character, for example, the constants c and c_1 and hence E and R would both be smaller than the calculated values for the quasi-isotropic substance without cement.[47]

[47] Voigt, Lehrb. Kristallphys., p. 964

Chapter XXIV. FLOW AND FAILURE

Non-reversing effects of pressure and stress

We have been considering only the self-reversing effects, that is, effects which disappear when the pressure or stress is removed. There remain to be considered the non-reversing effects, those which persist even though their original cause is gone.

Non-reversing effects from *uniform pressure* are rare in any substance, and none are known in silica. Its volume may change under pressure, and, if it be crystalline, its shape may change also, but when the pressure is released the original volume and shape are completely restored, as nearly as can be told by measurement.

Very different are the effects of non-hydrostatic stress—of non-uniform pressure, tension, or shear. The effects range all the way from the flow of liquid silica under its own weight to the crushing to powder of a quartz crystal under the immensely unequal compressive stress of a testing machine.

In a general way these effects may be differentiated according to the size of the units which are differentially displaced. If the units are so small as to be invisible, we call the effect *flow*. If they are large enough to be seen, we call the effect breakage or *failure*.

This classification may be further elaborated:

(A) Invisible displacements:
  (1) Displacement of atoms
  (2) Displacement of small atom-groups or of molecules
  (3) Displacement of large atom-groups or of groups of molecules

(B) Visible displacements:
  (4) Displacement of particles having colloidal size
  (5) Displacement of portions having colloidal dimensions in one or two directions only (laminae and fibers)
  (6) Displacement of easily visible portions.

The individual movement of parts in the first 3 types of non-reversing effects,—the "invisible displacements,"— can not be seen, but their general resultant can be studied through optical effects, study of vibrations, etc. Somewhere in this series, we may suppose, is the transition from true flow to plastic flow, but there is so little quantitative information on the character of the flow of silica that there is no need to go further into the subject here.

It must be understood that these types of displacement are not sharply divided but may grade one into another, and two or more of them may occur at once. But they may still be distinguishable, though occurring in the same substance at the same time.

The flow of liquid silica and vitreous silica

The liquid phase of silica is stable under atmospheric pressure only above 1710°C. At such temperatures it has the usual mechanical properties of a liquid, but a liquid of the type known as *viscous* or slow-flowing.

There is no logical reason to expect any sudden change in the mechanical properties of liquid silica as it cools below 1710°, and none has been observed. If crystallization to cristobalite or tridymite does not begin it remains a viscous liquid, becoming more and more viscous as the temperature falls.

Neither is there any reason to expect an abrupt change of properties from liquid to glass. The viscosity increases in geometric ratio for equal decrements of temperature. Under such a law of change an apparent discontinuity may be the result merely of the limited range of human perception. The difference between the "instantaneous" and the "life-long" is, after all, but a small fraction of the difference between the revolution-period of an electron and the age of the Earth. Hence the change from visible flow to apparently perfect mechanical stiffness may occur within a range of a few degrees, and still be only a part of a perfectly continuous temperature-viscosity curve.

The lower limit of easily measurable flow in vitreous silica is about 800°C.

Fluidity of liquid silica

No quantitative measurements have been made of the fluidity of liquid silica above 1710°. Qualitatively, the fluidity of fused silica near the melting-point is known to be very small, and it does not increase rapidly with temperature. Hence the difficulty of obtaining clear vitreous silica free from gas bubbles, for the liquid is so viscous that gas bubbles when once entrapped cannot escape.

In their experiments on fused silica Day & Shepherd[1] found that even at temperatures estimated to be in the neighborhood of 2500°C very small air bubbles would not rise through the liquid rapidly enough to let them all escape within a period of several hours.

Heraeus, on the other hand, found that fused silica could be made hot enough to increase its fluidity to the point where inclosed gas bubbles would rise. Since this was done in an iridium container, the temperature must have been below 2300°.

Day & Shepherd were dealing with fused powdered silica in which some of the bubbles were very small. Heraeus was melting quartz crystals, entrapping only a few relatively large bubbles. This is perhaps the reason for the apparent disagreement between the two observations. The temperature at which Heraeus' articles were blown he estimated to be over 2000°, and

[1] Article cited in VI, note [48].

thought that the glass might have reached 2300 to 2400° when being heated in the flame.[2] This estimate is probably too high.

Flow in glassy silica

There is no reason to expect any discontinuity in the properties of liquid silica at 1710°, the melting-point of cristobalite. Thermodynamically, glassy silica at room temperature is the same phase as liquid silica at a temperature so high that it flows like water. Nevertheless, because of the marked mechanical contrast between glass and liquid, it is desirable to consider the phenomena of flow in the glass as a separate division of the subject.

Two effects should be distinguished, at least in theory, though they cannot always be separated experimentally. These are: (A) Flow under external stress; (B) Spontaneous flow.

(A) Flow under stress may occur as the result of applied stresses that are easily measurable, as when a fiber is drawn or a bulb blown out of vitreous silica. Or the stresses may be small, such as those resulting from the action of the Earth's gravity on a fragment, tending to flatten it out; or of surface tension, tending to round it into a sphere. External stress would include also the stress exerted on one part of a fragment by another part, due to unequal rates of cooling of the two parts from a fluid state. Such stresses cause most of the strain seen in unannealed fragments of glass.

(B) Spontaneous flow results from internal rearrangements among the atoms or atom-groups. Such rearrangements can occur, of course, without producing any change of shape of the fragment, that is, without producing any flow, but it usually happens that detectable flow is one of the results. If a fragment can be imagined free from strain and from surface tension, and travelling through interstellar space as a free object, it would still be liable to change of shape by spontaneous flow, though subject to no so-called "physical" force except the mutual gravitation of its atoms. The non-gravitational attractions and repulsions of atoms are chemical forces, and it is these that cause spontaneous flow.

Flow of both kinds occurs in vitreous silica at all temperatures down to room temperature, and perhaps lower.

Experimental evidence of flow

At 1350° a "rather thickwalled" vessel can stand for hours under external pressure of an atmosphere (vacuum inside) without being noticeably deformed, while at 1500° it is distinctly deformable by small forces.[3]

Joly[4] made some rough measurements in 1900 on the temperature of visible flow of vitreous silica. He heated a fiber of the glass, 0.0136 mm in

[2] Heraeus, W. C., article cited in VI, note [12].
[3] Heraeus, article cited.
[4] Joly, J., Proc. Roy. Dublin Soc. (1900) 9: 298-303.

diameter, by partly surrounding it over a length of 10 cm with a platinum trough 1.5 mm square heated by means of an electric current. When the trough was at 850°C the fiber yielded 0.76 mm in 55 minutes and a further 0.39 mm in 35 minutes, under a load of 293 kg per sq. cm. Extension continued under this load until the fiber broke. The fiber was undoubtedly at a lower temperature than 850°.

Joly also reported that further experiments, using a platinum tube and stronger fibers, "appeared to reveal slow extension at still lower temperatures" but no further quantitative data were forthcoming.

From these experiments on vitreous silica fibers Joly[5] concluded that an excess of pressure of 1 atmosphere in a spherical bulb 10 mm in diameter with wall 0.25 mm thick would increase the volume of the bulb by 0.1 per cent in 83 hours at 785°, in 40 hours at 870°, or in 8 hours at 920°.

In the course of his interferometer measurements of the thermal dilatation of vitreous silica Randall[6] observed distortion of the base-plate and cover-plate, both of which were of vitreous silica. The originally plane surfaces ceased to be plane, as shown by the change of shape of the interference fringes, and the distortion was permanent. There was no distortion in several hours at 940° or lower.

Evidence of a slow flow under surface tension is found in an experiment by Joly,[7] in which powdered vitreous silica heated for 35 days in a closed unglazed porcelain crucible at a temperature just under the melting point of gold (1063°) showed rounding of the edges of the fragments accompanied by devitrification.

Threlfall & Pollock[8] observed what appeared to be the slow flow of vitreous silica at atmospheric temperatures. They employed a silica thread 0.038 mm in diameter and 305 mm long, stretched horizontally by a spring, and supporting at its middle point a light lever whose center of gravity is a little to one side of the thread. The twisting moment due to this lever is counterbalanced by a twist in the thread of about three complete turns at each end, changes in the force of gravity being then measured in terms of the additional twist required to bring the lever to a definite position.

The daily rate of change in the equilibrium position under the conditions stated (equivalent to a shear strain of about 0.0048, see p. 453), for a thread mounted in September, 1896, was 2.5 minutes of arc (in a total of 3×360 degrees) in September, 1897, and 0.3 minute in September, 1898.[9] After being continuously under tension for 28 years, this same thread now shows no observable drift in the course of a month.[10] The observations do not furnish conclusive proof of flow in the silica thread, for effects of this magnitude may take place in the end supports;[11] but in view of the fact that the fastening was made by silvering and copper-plating the thread and then soldering it to metal, it seems probable that a part at least of the drift was in the silica.

[5] JOLY, J., article cited in VI, note [40].
[6] Article cited in XX, note [65].
[7] Article just cited.
[8] THRELFALL, R., & POLLOCK, J. A., *On a quartz thread gravity balance,* Phil. Trans. Roy. Soc. London (1899) A, **193**: 215-258.
[9] p. 247 of article cited.
[10] Personal communication from Professor THRELFALL.
[11] Personal communication from Dr. TUCKERMAN.

On the other hand, Griffith [12] has maintained a vitreous silica fiber for a week at room temperature under an elastic extension of 5 per cent without detecting any flow, although a change of 0.005 per cent could have been detected. The stress-difference in this fiber far exceeds that which would cause rupture in any crystalline substance.

Linear changes in vitreous silica

The lengthening or shortening of vitreous silica rods and tubes after heating is probably a case of permanent change either of shape or of density. These effects are frequently referred to as "hysteresis"; but wrongly so, for true hysteresis is a reproducible phenomenon. The changes dealt with here are not due to hysteresis or to delayed dilatation (see p. 368) but are *permanent* changes either in density or shape, or both. Whether the lengthening (or shortening) is partly or wholly a simple change of shape of the rod or tube, due to flow, or whether it is partly or wholly due to a change of density, cannot be stated positively, since the measurements are linear only. It is probably a case of what I have called spontaneous flow (p. 474), unaffected by gravity, surface tension, or mechanical strain.

Such linear effects have been observed by Callendar, Randall, and L. F. Richardson.

According to Callendar [13] a permanent *lengthening* begins at 1000° and continues at all temperatures up to 1400° and above, the length at room temperature after cooling being found greater than it was before heating. This lengthening is superposed upon and independent of the reversible (positive and negative) dilatations at these temperatures.

In the course of his interferometer measurements of the thermal dilatation of vitreous silica Randall [14] observed a continuous lengthening of the glass ring, which continued for an hour after the normal period for attaining constant dilatation. The lengthening showed no indication of decreasing rate. At 940° and lower the ring reached a constant dilatation well within an hour, without further continuous change.

L. F. Richardson [15] observed only *shortening* of the bars which he tested, when studying the suitability of vitreous silica as a material for length standards. End-measure rods of both transparent and translucent silica, about 45 cm long, previously annealed, were exposed to temperatures of —190 to 400°C for periods of 1 to 90 hours, and the lengths measured a few hours after cooling. Those heated to temperatures (t) up to 400° showed a linear shrinkage ranging from zero [precision not stated] up to $5 \times 10^{-9}t$. Heated to 800°C, there was a shrinkage of $17 \times 10^{-9}t$. These represent changes in volume amounting to 0.2 to 2 per cent of the mean dilatation-coefficient; or, if they

[12] Jeffreys, H., *The Earth* (1924, Cambridge) p. 278.
[13] Article cited in XX, note [55].
[14] Article cited in XX, note [66].
[15] Kaye, G. W. C., *A silica standard of length,* Proc. Roy. Soc. Lond. (1911) **A 85**: 430-447; Coll. Res. Natl. Phys Lab. (1912) **8**: 87-105.

are simply changes in shape, they are 0.2 to 2 per cent of the mean linear expansion-coefficient of the rod.

A more exacting test than those just quoted was made on the vitreous silica standard meter of the National Physical Laboratory.[16] After having been constructed and carefully compared with an invar meter, it was heated up during 2 days to 450°, held there for 8 days, and then cooled during 14 days. The resulting permanent change in length was a shrinkage of 0.7 μ, that is, less than 1 in a million. In terms of the temperature of annealing, for comparison with the preceding data, it corresponds to $1.6 \times 10^{-9}t$.

A change of volume in vitreous silica bulbs may be found from the ice-point measurements of Harlow,[17] from which I have calculated the following:

t = max. temp. to which bulb was heated	Change of volume
100°	Increase, of less than $15 \times 10^{-9}t$
184°	" " " " $10 \times 10^{-9}t$
300°	" " " " $6 \times 10^{-9}t$

In almost every case the ice-point indicates a permanent *increase* of volume, but of a magnitude almost too small to measure.

Absence of any observable change of volume has been noted by C. B. James,[18] in measuring the dilatation of mercury with a 100-cc cylindrical vitreous silica bulb. Measurements of its volume at 0° showed that heating to 100° or cooling to —38° produced no change in volume greater than the equivalent of 0.07 g mercury in 1527 g, or 1 in 20,000, which is equivalent to, at most, $1 \times 10^{-6}t$. This is of about the same magnitude as the thermal dilatation itself, so the test does not prove much about the constancy of volume of the silica.

Accommodation

A torsional effect having the character of a permanent change of structure, and possibly of dimensions, under stress at room temperatures is the effect known as "accommodation." It was first discovered by Weber and has been studied by Kelvin, Bouasse, and others. The phenomena are as follows:

When a weight suspended by a fiber or wire is given a slight twist and then released it begins to oscillate about the axis of the fiber. The relations between the period, amplitude, and decrement of amplitude with time are at first variable, but after a great many oscillations the fiber or wire seems to reach a permanent state in which constant relations between the quantities mentioned can be experimentally reproduced. The initial stage of variability is the "accommodation" stage. The phenomenon is known also in other kinds of distortion and in many other materials.

Guye & Einhorn observed such accommodation in fibers of vitreous silica, and their experiments, described in the preceding chapter, were all made after preliminary oscillations had been kept up for two days.

[16] KAYE, article just cited.
[17] HARLOW, articles cited in XX, notes [79] and [86].
[18] Article cited in XX, note [77].

Another and very different example of the slow action of a mechanical stress is found in the fact noted by Kaye [19] that although very fine lines can be ruled with a diamond on a polished surface of vitreous silica, the lines are of little use for precision measurements such as comparison of length standards, because the edges of the lines shell or flake off within a day or two after the ruling is done.[20]

Flow in quartz

I do not know of any convincing evidence of flow of any kind in crystalline quartz.

Joffé & Kirpitcheva [21] have followed the effects of compressive stress on a sodium chloride crystal by means of Laue X-ray photographs of the crystal. Most of the original Laue spots elongate into lines composed of many spots close together, although the spot corresponding to the rhombic dodecahedron {110} remains unchanged. This indicates that the crystal flows by breaking up into many small crystals a few hundredths mm in diameter but having the same structure as the original; these fragments slide along {110} planes, at the same time rotating by various amounts.

Under similar conditions there is no change in the spots given by quartz until it breaks to pieces.

The question of surface flow

Considerable discussion has been aroused recently by Beilby's [22] book, in which the author builds up a strong case for the conversion of crystalline metal into amorphous metal by polishing, as well as by distortion of various kinds.

Beilby has extended his experiments to quartz, and has observed that the surface layer produced on quartz by the usual methods of polishing differs in some way from the underlying crystal. "If a drop of commercial hydrofluoric acid is placed on the polished surface of a lens of rock-crystal, it spreads slightly and then becomes surrounded by what looks like a halo of condensed vapour. Under the microscope it is seen that the halo is caused by the penetration of the acid *under* the vitreous surface layer. The outer or most advanced portion of the halo is minutely granular. As the outer edge of the drop and the inner edge of the halo are approached, the granules become larger till they assume the appearance of minute hemispherical droplets. As the halo steadily grows by the penetration of the liquid, the droplets immediately surrounding the large drop become larger and larger till they encroach on each other and finally coalesce. When the central drop is removed by touching it with the torn edge of filter-paper, the film of liquid which had penetrated under the surface layer gradually returns towards the spot which had been occupied by the drop, and there evaporates. With the retiral of the penetrating liquid, the disturbed layer subsides and becomes perfectly flat."

[19] Article cited.

[20] The phenomenon is known also in ordinary glasses. (Personal communication from Dr. Tuckerman.)

[21] Joffé, A. F., & Kirpitcheva, M. v., Phil. Mag. (1922) **43**: 204-206.

[22] Beilby, G., *Aggregation and flow in solids* (1921, London).

Photomicrographs show that the acid removes a surface layer and reveals a surface covered with scratches, which have apparently been covered over or filled up by a surface flowage during polishing.

We are dealing here not with the undeniable evidence of measurable changes of shape, but with appearances, which it seems to me can be explained more reasonably than by Beilby's assumption that quartz has been mechanically converted into amorphous silica on the surface of the lens. A layer of very finely divided quartz could give the phenomena seen by Beilby. Quartz ground under water for 4 hours settles and compacts into a cake with a reflecting surface, yet contains no amorphous silica visible under the microscope.[23]

If the polishing is done in presence of water, as it nearly always is, then it is conceivable that hydration of some of the silica may also occur, yielding a partly amorphous layer. But this amorphous silica would be due to chemical reaction and not to mechanical effects.

From his experiments on the polishing of metals, glass, and quartz, Beilby has concluded that "The grinding of crystalline substances to powder does not simply consist in their reduction to finer and finer crystalline fragments, but it involves the transformation of, at any rate, a part of the substance into the vitreous condition."

No support for this hypothesis can be found in the data on the density of finely ground quartz (see p. 299). Johnston & Adams' experiments show that if the density of such vitreous material be taken to be the same as that of vitreous silica, then the amount of it produced by grinding to a size of 20 μ is less than 0.15 per cent, if any.

In the experiment just cited, also, no amorphous silica can be seen under the microscope in quartz ground for 4 hours under water in an agate mortar in a mechanical grinder. Ray's experiments on this subject have been shown to be unreliable (see p. 300).

Similarly, experiments with the low-density cristobalite obtained from chalcedony, etc. (see p. 304), show that the only effect of very fine grinding is to *raise* its density instead of lowering it towards that of amorphous silica. This is not as good evidence as the quartz case, however, because other factors enter in the case of cristobalite.

Mechanical strength

There are no accepted general principles relating to the breaking strength of substances under stresses of different kinds. The force per sq. cm required to crush, or pull apart, or twist apart a specimen of a substance is known to vary with experimental conditions, such as the size and shape of the specimen and the rate of application of the force; and, furthermore, the strength under one kind of stress is not generally predictable with any accuracy from the strength under another kind of stress.

Nevertheless, for each particular kind of stress (crushing, tension,

[23] Unpublished experiments by F. Hastings Smyth, Geophysical Laboratory, 1923.

bending, torsion, penetration) there are, within liberal limits, certain constant breaking strengths which are characteristic of the substance.

For a brittle substance such as silica the strength constants may be defined as follows:

(1) Crushing strength: The force per sq.cm of cross section of the specimen, exerted on the polished parallel faces of a right cylinder or prism, when the specimen explosively crushes to powder.

(2) Tensile strength: The force per sq.cm of cross section, measured at the narrowest part of a rod of the material, when the rod breaks.

(3) Bending strength: for a bar of brittle material, such as silica, this is usually stated in terms of the *modulus of rupture*, B, defined by: $B = MC/I$, in which M is the bending moment which ruptures the bar; I is the moment of inertia of the cross-section about the axis of bending (which is through the centroid of the section in the simpler cases; and C is the distance of the farthest "fiber" in tension from the axis of bending. For a square bar h cm high and b cm wide resting on two parallel edges l cm apart and loaded at the middle with a force p, the formula becomes: $B = \frac{3}{2} \cdot \frac{l}{bh^2} p$.

Mechanical strength of silica

Only quartz and vitreous silica have been studied experimentally.

Crushing strength

The crushing strength of quartz when compressed in the direction of the principal axis is about one-tenth greater than perpendicular to the axis. Quartz has two or three times the crushing strength of high-carbon steel and a hundred times that of most building stone or concrete.

Vitreous silica has a crushing strength about one-fifth less than that of quartz. It is two or three times as strong as ordinary glasses, and a fourth to a half stronger than the strongest borosilicate glasses.

Tensile strength

Like other crystals and glasses, silica under the usual methods of testing has a tensile strength which is very much smaller than its crushing strength.

The tensile strength of quartz parallel to the axis is greater than that perpendicular thereto, just as with the crushing strength. The strength parallel to the axis is from 30 to 100 per cent greater than that of ordinary glasses, and 40 per cent greater than the strongest optical glass.

The tensile strength of vitreous silica seems to be genuinely variable and not merely uncertain because of the uncertainties of testing.[24] Its properties will be more fully discussed at a later page.

[24] Dr. Tuckerman, who has had much more experience than I with the vagaries of testing machines and test specimens, doubts this statement.

Bending strength

The bending strength of quartz shows the same kind of difference between parallel and perpendicular directions as do the tensile and crushing strengths. Logically, the bending strength can be calculated directly from the tensile strength, or vice versa. Practically, the relation does not hold very closely, because certain assumptions made in the calculation are only approximately true, and also because the tensile test searches out the accidental flaws of the specimen more thoroughly than does the bending test, especially the test with a central load. Thus the bending strength of quartz, as determined experimentally, is one-fourth to one-half greater than that deduced from the tensile strength.

A general summary of values is contained in Table XXIV.1.

TABLE XXIV.1.

STRENGTH OF QUARTZ AND VITREOUS SILICA AT ROOM TEMPERATURE.

Unit of stress is the kilomegabarye (10^9 dyne per sq. cm). For equivalence of units see Table XXII.1.

	Quartz		Vitreous silica
	∥ to axis	⊥ to axis	
CRUSHING STRENGTH			
Strength usually to be expected in small specimens	24	22	19.5
Maximum observed	27.2	26.85	22.6
TENSILE STRENGTH			
Strength usually to be expected in small specimens carefully centered	1.1	0.83	3 to 8
Maximum observed	1.19	0.91	11.5
MODULUS OF RUPTURE (BENDING STRENGTH)			
Strength usually to be expected	1.35	0.90	
Maximum observed	1.76	1.30	0.675

THE EXPERIMENTAL DATA

The most recent, and apparently the most dependable, measurements of the mechanical strengths of quartz and vitreous silica are those of Berndt.[25] Other determinations on quartz have been made by Rinne and by Voigt. Berndt's measurements are summarized in Table XXIV.2, in his original units. (See Table XXII.1 for conversion factors.)

[25] BERNDT, G., Verhandl. Deut. Physik. Ges. (1917) **19**: 314-327. Same (1919) **21**: 110-117.

Rinne[26] obtained a maximum crushing strength for quartz compressed in the direction of the axis of 15,364 kg per sq. cm or 15.066 kilomegabaryes. The cubes were 1 cm on an edge, cut from a crystal from St. Gotthard, and were optically homogeneous.

Voigt[27] made an elaborate series of tests on the bending strength of quartz, using bars of quartz about 30 mm long by 2.5 mm square, the middle portion of each bar being ground and polished to a minimum cross-section of about 2.2 x 2.2 mm. The stress was applied at the extended ends of the bar, with the middle supported on two knife-edges 12 mm apart.

In a substance of trigonal trapezohedral symmetry, such as low-quartz, the side faces of a long prism of square cross-section are equivalent only if the long direction of the prism is perpendicular to a twofold symmetry axis while at the same time the side faces are at 45 degrees to that axis. Equivalence of faces in such a prism is desirable because experiments on sodium chloride have shown that the strength of a prism varies with the crystallographic orientation of its faces.

TABLE XXIV.2.

SUMMARY OF BERNDT'S DETERMINATIONS OF MECHANICAL STRENGTH.

Data are in kg per sq. cm.

	Total number determinations	Number rejected	Maximum strength	Average strength
Compression:				
Quartz, ∥ to axis	29	20	28,020	24,470
Quartz, ⊥ to axis	32	19	27,380	22,780
Vitreous silica	11	2	23,000	19,700
Vitreous silica containing bubbles	10	3	21,500	19,900
Tension:				
Quartz, ∥ to axis	4	2	1,210	1,160
Quartz, ⊥ to axis	6	1	930	850
Bending:				
Quartz, ∥ to axis	5	0	1,790	1,400
Quartz, ⊥ to axis	5	0	1,180	920

Most of Voigt's prisms were oriented in accordance with the principle above stated. A few having other orientations were also tested, but the variability of the bending strength from specimen to specimen was more than enough to conceal any real difference due to orientation.

Voigt's original data are summarized in Table XXIV.3. The prisms in each set are oriented alike. *a* indicates a twofold (equatorial) axis and *c* the threefold (principal) axis.

It is evident from the Table that the tensile strength as revealed by bending is distinctly greater for the axial direction than for the equatorial, and that intermediate directions show values between the maximum and the minimum.

For the bending strength of vitreous silica Schulze[28] obtained the value 675 kilomegabaryes on a bar $2.72 \times 10 \times 100$ mm, containing a few bubbles.

[26] RINNE, F., Centralbl. Mineral. **1902**: 262-266.
[27] VOIGT, W., Ann. Phys. u. Chem. (Wiedemann) (1893) **48**: 663-673.
[28] Article cited in XXIII, note [20].

TABLE XXIV.3.

TESTS OF BENDING STRENGTH OF QUARTZ. VOIGT, 1893.

Unit of stress is kg per sq. cm. (See Table XXII.1.)

Set No.	Orientation of prism		Breaking stress	Mean	General mean
	Length	Side			
Maximum stress ‖ to axis					
I	$\perp a, \parallel c$	45° a	1650 1690 1480 1640 1630	1620	
VII	$\perp a, \parallel c$	$\parallel a$	1730 1740 1520 1630	1660	1630
Maximum stress ⊥ to axis					
IV	$\perp a, \perp c$	45° a	1270 1210 1270 1300	1260	
VIII	$\perp a, \perp c$	$\parallel a$	1290 1500 1210 1290 1310	1320	1295
IX	$\parallel a, \perp c$	$\parallel c$	1260 1350 1270 1300	1300	
Other orientations					
II	$\perp a$, 30° c	45° a	1720 1640 1230 1250 1810 1270	1490	
III	$\perp a$, 60° c	45° a	1240 1070 1240 1210	1190	
V	$\perp a$, 120° c	45° a	1570 1410 1560 1590 1350	1500	
VI	$\perp a$, 150° c	45° a	1610 1460 1430 1410	1480	
X	45° a, 45° c	$\parallel a$	1420 1510	1470	

Heymans & Allis[29] found 420 kilomegabaryes on a bar from the General Electric Company.

Effect of conditions of testing

Winkelmann & Schott found that the apparent crushing strength of glasses increased with the size of the cubical specimen. Berndt[30] found just the opposite effect, using both cubes and cylinders. The question remains open.

Bauschinger found the crushing strength of sandstone cubes to be independent of size.

Berndt observed no effect due to varying speed of application of the pressure in the crushing strength of glass.

In general, all the accidental errors which affect measurements of compressive, tensile, or bending strength tend toward low values. The maximum observed, therefore, is the most likely to be correct, and there is little objection to rejecting all unusually low values as unrepresentative.

Manner of failure

Compression.—Some of the quartz specimens tested by Berndt spalled and splintered before crushing. The 3 splintered specimens of those crushed parallel to the axis had the same average strength as the 6 unsplintered. Of those perpendicular to the axis, the 7 splintered specimens averaged 3½ per cent stronger than the 6 unsplintered.

A typical 1-cm cube in Rinne's experiments cracked at about 11.3 kilomegabaryes before crushing explosively at about 15. The crushing was sudden and violent, causing a scattering of the fragments.

Only 3 out of Berndt's 16 vitreous silica specimens remained unsplintered before bursting, but their average strength was the same as that of the splintered specimens.

Tension.—Berndt observed that the failure of quartz in tension took place by the breaking out of a wedge from the middle of the rod, with its faces at about 45° to the axis of the rod.

In Threlfall's experiments[31] the failure of fine vitreous silica threads in tension was splintery, a perfect sharp point being produced in one case.

Tensile strength of vitreous silica

The tensile strength of vitreous silica fibers or of glass fibers in general has been found to vary more or less consistently, and quite widely, with several variables. The most important of these are:

(a) The diameter of the fiber
(b) The age of the fiber
(c) The maximum temperature to which the glass has been heated
(d) The temperature of the glass during the drawing out of the fiber.

[29] Article cited in XXIII, note [14].
[30] Berndt, first of articles cited in note [25].
[31] Article cited in XXIII, note [7].

Influence of diameter

It has long been known that fine wires are stronger per unit of cross-section than thick wires, and the same is true for fibers of glass. A very fine fiber may have as much as 20 times the tensile strength of a rod. A part of this difference,—but not all,—arises from the ordinary conditions of testing, because the rod is very short compared with its length and is hard to mount so that the stress is purely axial; while the fine fiber accommodates itself easily to a slight bending.

The widest range of strength with diameter reported for silicate glasses is that found by Griffith.[32] A decrease of diameter from 1.0 mm to 0.0033 mm (3.3 μ) increased the tensile strength of a certain silica-alumina-potash-lime glass from 1.717 to 33.85 kilomegabaryes. Although a similar series was not made on pure vitreous silica, yet fine vitreous silica fibers of equal or greater strength were obtained, and since the tensile strength of vitreous silica rods is of the order of 1 kilomegabarye there is every reason to believe that a similarly large range of strength would be found for vitreous silica fibers.

Boys[33] observed that the tensile strength of vitreous silica fibers per unit cross-section increases as the fibers become smaller, not only for drawn fibers but for fibers reduced in diameter by partial solution in hydrofluoric acid. In other words, a given load in grams will break a fiber of a certain diameter whether it be a fresh fiber or one reduced to that diameter by solution. Threlfall[34] also observed a considerable increase in strength with diminishing diameter. Their results are given in Table XXIV.4.

TABLE XXIV.4.

DATA ON THE TENSILE STRENGTH OF VITREOUS SILICA FIBERS.

Diameter of fiber mm	Breaking load grams	Breaking strength Kilomegabaryes	Observer
0.036	34.34	3.37	Threlfall
0.020	10.2	3.25	Threlfall
0.0175	....	8.0	Boys
0.016	10.5 } 12.25	6.08	Threlfall
0.016	14.0 }		
0.014	10.		
0.014	9.2		
0.014	9.2 } 9.42	6.12	Threlfall
0.014	11.7 }		
0.014	8.2		
0.014	8.2		
0.0048	....	11.5	Boys

Influence of age

Griffith[35] noticed that vitreous silica fibers are very much stronger for a few minutes after they have been drawn than they are later.

[32] GRIFFITH, A. A., Phil. Trans. Roy. Soc. Lond. (1920) **221**: 163-198.
[33] Article cited in XXIII, note [28].
[34] Article cited in XXIII, note [7].
[35] Article cited.

Griffith's experiment showing this temporary high strength was confirmed by Rayleigh,[36] who drew a small rod, bent it to a large angle and marked the curve on paper, then stroked it with another silica rod and bent it again, whereupon it broke long before reaching its first curvature.

Effect of heating

The most extensive tests of the effect of heating upon the strength of vitreous silica at atmospheric temperatures are those of Blackie,[37] made in 1908. His strength tests were all made by bending bars 1 to 3 mm thick and 5 to 10 mm wide between knife edges 15 mm apart. The results are contained in Table XXIV.5.

TABLE XXIV.5.

TRANSVERSE BREAKING STRENGTH OF VITREOUS SILICA BARS. BLACKIE, 1908.

(Each figure is an average of about 10 determinations. Average deviation from mean is 10 to 20 for U, G, and S; somewhat greater for T.)

Mean t at which heated ° C	Period of heating, hrs.	Modulus of rupture in kg per sq. cm			
		U	G	S	T
Unheated	....	342	382	281	902
1124	8	376	310	319	818
1122	3½ + 4½	358	337	307	750
1188	4	425	309	285	897
1186	8	369	311	277	802
1275	4	257	270	211	745
1353	4	218	186	188	339

U = Unglazed, strips cut from rods. Opaque or translucent silica. Contains long parallel-sided bubbles.
G = Glazed strips cut from rods similar to preceding. Opaque or translucent silica.
S = Satin-surfaced on one side, with flat elliptical bubbles; rough on other side, with adhering sand-grains. Opaque or translucent.
T = Bars formed by collapsing the walls of tubes by heating. Transparent, with few long bubbles.

The decrease in strength due to heating is undoubtedly allied to the spontaneous flow and the changes in elastic constants which occur in vitreous silica at higher temperatures. According to the theory in XV these changes are due to the gradual rearrangement of the atom-triplets into the cristobalite pattern.

The change may progress so far that the glass becomes quite brittle when cold, and yet it may give no outward appearance of devitrification until cooled below the inversion temperature of cristobalite. This observation led Endell & Rieke [38] to suggest that the life of vitreous silica

[36] Article cited in VIII.
[37] Article cited in XX, note [93].
[38] Article cited in VI, note [41].

apparatus at high temperatures might be considerably lengthened by not allowing the silica to cool below about 300 or 400°.

In 1912 F. Thomas [39] published results of experiments purporting to show that specimens of vitreous silica containing small percentages of ZrO_2 or of TiO_2 are stronger in bending and crushing than pure vitreous silica, but the data vary over such a wide range that I do not believe such a conclusion is warranted.

Koenigsberger used some tubes of these special glasses for experiments on the critical phenomena of mercury, and his reports were interpreted by some readers as indicating that the special glasses are stronger, but Koenigsberger [40] himself disclaimed any such conclusion, pointing out that the size of the capillaries used was a much more important factor than the composition of the glass.

Gliding

A peculiar kind of flow exhibited by many crystalline substances is that known as *gliding*. Under the action of a stress a portion of the fragment will move as a whole into a new position, while the crystallographic and other axes may take up different directions from those occupied in the original fragment. The displaced portion moves as if planes of atoms slid over one another, sometimes with simultaneous rotation, as shown by the change of symmetry.

The plane thus marked as of special character, and defined by reference to the original axes, is called a *gliding-plane*.

When subjected to the stresses due to unequal cooling or to direct non-uniform pressure, low-quartz exhibits gliding-planes parallel to the primary positive and negative rhombohedrons (r and z) and to the hexagonal prism, m. No other gliding-planes have been observed.

Cleavage

Failure in an amorphous substance produces surfaces of separation between the fragments which are irregular or curving. Failure in a crystalline substance also produces such surfaces, but in addition may give rise to surfaces of separation which are not only plane but which have all the qualities of faces produced by free growth of a crystal. Such planes, whose position is defined in the same way as the natural faces (see XII), are called *cleavage-planes*.

Since all the faces of a crystal-form (see p. 184) are physically equivalent, all the planes of cleavage parallel to such a set of faces should be producible with equal ease, and such is found experimentally to be the case. The crystal-form and the cleavage-form may be described in the same terms.

[39] Article cited in VI, note [46].
[40] Article cited in VI, note [53].

The *character of the cleavage* is a qualitative property which states the relative ease with which a given cleavage can be produced mechanically. "Perfect" and "imperfect" are the usual distinctions.

Quartz

The cleavage of low-quartz is not distinct in any direction. When broken by shock or stress, the crystal usually breaks with a conchoidal fracture. Where plane surfaces of separation have been observed, they have nearly always been parallel to the primary positive or negative rhombohedron or to the hexagonal prism.

There is some question whether low-quartz has any true cleavage whatever. The occasional plane fracture surfaces may be only the result of gliding-planes (see p. 487), as suggested by Lehmann and by Judd.

Whether caused by true cleavage or by gliding-planes, the separation is easiest and most distinct parallel to the primary positive rhombohedron, and somewhat less distinct parallel to the negative rhombohedron. Separation parallel to the hexagonal prism or to the base is much less distinct than to either of the rhombohedrons.

Experimental evidence

The relatively greater importance of the rhombohedral cleavages is well shown by the cleavage of a very thin plate cut parallel to the principal axis and perpendicular to a prism face. Such a plate can be cleaved by pressure with a pin point, as described by Mallard.[41] The separation parallel to the two rhombohedrons yields straight cracks across the plate, perpendicular to its surface and making an angle between themselves of 72° 26′. The surfaces so formed are plane and reflect like any crystal face, the positive rhombohedral surface being distinctly more perfect than the negative.

Very different are the separations parallel to the prism and to the base. The cracks appear perfectly straight, but do not give reflecting surfaces. On close examination they are found to be microscopically serrated, the crack as a whole consisting of alternating planes parallel to the positive and negative rhombohedrons, respectively. This kind of cleavage is analogous to the fibrous cleavage of gypsum, which is apparently parallel to $\{\bar{1}01\}$ but in reality consists of a combination of two cleavages parallel to $\{\bar{1}11\}$.

No other lines of separation are visible in a thin plate broken by means of a pin point.

According to the experience of Japanese quartz workers, fracture surfaces sometimes occur not only parallel with the rhombohedrons and hexagonal prism, but also the common trigonal pyramid and trapezohedrons. This has been shown by etching by Ichikawa.[42] There is also an imperfect cleavage parallel to the second-order prism, $\{11\bar{2}0\}$. The fracture of quartz perpen-

[41] Mallard, E., *Sur les clivages du quartz,* Bull. Soc. Franc. Min. (1890) **13**: 61-62.

[42] Article cited in XXV, note [39].

dicular to the principal axis is more regularly conchoidal than the fracture in other directions.

So-called primary quartz is more brittle than secondary quartz, as shown by the fact that the Japanese quartz sculptors at Kofu distinguish between the brittleness of rock crystal from pegmatite in the granite of Kinbuzan and rock crystal from veins in the spotted clay slate formed in contact with granite at Takemori.[43]

Their experience also seems to show that quartz which has been ignited is less brittle than before ignition. This statement presumably applies to smoky or colored quartz which has been heated to decolorize it.

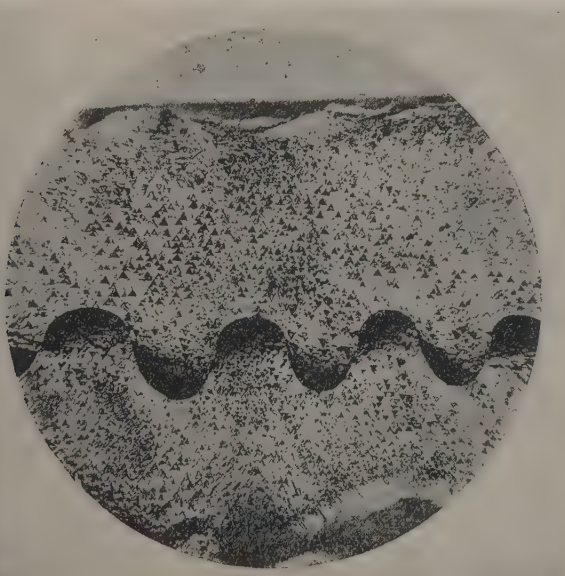


FIG. XXIV.1.—Crack produced by the 573° inversion in a plate parallel to the base. Transmitted light. Magnified. (After Mügge.)

Failure in quartz is often produced by the stresses set up during its inversion from low-quartz to high or vice versa. Mügge[44] found that the cracks formed bear a distinct relation to the newly-formed twinning boundaries resulting from the inversion. The cracks, in general, run parallel to the positive rhombohedron $\{10\bar{1}1\}$. The twinned areas follow the same course in a general way, though the boundaries in detail are sometimes very irregular.

An effect produced in a plate parallel to the base is of especial interest. A detail of such a plate after etching is shown in Figure XXIV.1. The upper boundary in the picture is parallel to the hexagonal prism $(10\bar{1}0)$. The crack

[43] ICHIKAWA, article cited.
[44] Article cited in VII, note [3].

has the form of a sine-curve running parallel to (10$\bar{1}$0). Etching shows that a belt of quartz following the sine crack is in reversed position with respect to the material on either side.

This "sine-curve" form of fracture has been observed also by Nacken [45] in spheres of quartz used in some preliminary experiments on high-temperature etching, but Nacken found that the fracture did not necessarily occur at the inversion-point. In a sphere of about 10 mm diameter it occurred at only a little above 100°, when the sphere was heated rapidly.

Cleavage of other modifications

Crystals of low-tridymite and low-cristobalite, as usually obtained, are not homogeneous crystals but aggregates of units too small for a determination of their cleavage. No observations on the high-modifications are known to me.

Hardness

The word "hardness" is used for a number of different ideas, most of which are not very exactly definable in terms of the true physical constants of a substance.

Hardness can be tested only by methods that leave a permanent effect in the specimen. The various kinds of hardness describe the resistance of the material to scratching, scraping, grinding, digging, and the like, involving the mechanical strength of the material in addition to its elasticity; involving also its fluidity and plasticity, if it possesses those qualities in appreciable degree.

Hardness is thus a quality which can be defined only by exact specifications of the manner of testing; hence there are as many kinds of hardness as there are ways of testing it.

Auerbach has suggested that the elementary ideal of a hardness test is a static test—the mark made by an object, say the finger-nail, pressed against a surface of the substance tested. But such a mark is small and difficult to examine, so the tester drew the object across the surface and made a scratch—a dynamic test. Only after years of experience and comparison has it become evident that the dynamic tester was on the wrong track, so far as static hardness is concerned. The multiplication of data only increased the confusion, because of the uncertain and variable effects of the speed at which the moving object is driven. An effort was therefore made by Auerbach to get back to a more nearly static test.

Nevertheless, the scratch or corrasion tests are so convenient and give such practically useful information about the properties of materials that they cannot lightly be set aside. They furnish what amounts to a test of mechanical strength on a very small scale, but it is a test which must be considered strictly as an empirical comparison between materials, and not a measure of any clearly definable property.

[45] Article cited in XII, note [8].

Two principal types of such hardness tests may therefore be distinguished: (1) indentation hardness or *penetration hardness;* (2) abrasive or *scratch hardness.* For a brittle substance like silica, scratch hardness is the type of most interest, but the existing data on both types of hardness will be briefly presented.

Penetration hardness

Auerbach [46] made a careful study of the problem of hardness in brittle substances, and determined on a penetration method. Using two pieces of the material to be tested, one having a spherical surface and the other a plane surface, he measured the force necessary to press the sphere into the plane until failure or permanent change was produced. The diameter of the surface of contact was measured at the same time. The ratio p/a^3 (in which p is the total pressure and a the diameter of the surface of contact) is found to be constant at all pressures (see modulus of penetration, p. 437), so that at the moment of failure only the limit pressure P needs to be read. Further, the introduction of a suitable function of r (the radius of curvature of the spherical surface) gives a constant which is independent of r. This permits the hardness to be defined by the formula

$$\text{Hardness} = \frac{6}{\pi}\sqrt[3]{Pr\left(\frac{p}{a^3}\right)^2}$$

The indentation-hardness of quartz and vitreous silica as determined by Auerbach's method [47] is given in Table XXIV.6.

Table XXIV.6.

Indentation-Hardness of Silica, by Auerbach's Method.

	Kilomegabaryes (10^9 dyne per sq. cm)
Quartz, plate perpendicular to principal axis	30.2 ± 0.9
Quartz, " parallel " " "	22.5 ± 1.1
Vitreous silica	21.9 ± 0.7

The degree of agreement among a set of determinations of the indentation-hardness is shown in Table XXIV.7. Although the agreement between successive tests is better than is usually the case with crushing and tensile tests, yet the variability is great enough so that one cannot say with confidence from the data in the Table that the penetration-hardness of quartz parallel to the axis is really greater than that of vitreous silica, although that of quartz perpendicular to the axis undoubtedly is greater than that of vitreous silica.

[46] Auerbach, F., Ann. Phys. u. Chem. (1891) **43**: 61-100. Smithson. Rept. **1891**: 207-236. Also Ann. Phys. u. Chem. (1896) **58**: 357-380.
[47] Auerbach, F., Ann. Physik (1900) **3**: 116-119.

TABLE XXIV.7.

VARIATIONS IN THE MEASUREMENT OF PENETRATION-HARDNESS OF QUARTZ, ON PLATE PERPENDICULAR TO AXIS (AUERBACH).[48]

Unit of pressure is kg per sq. mm.

First specimen, original series.			
$r = 1$ mm	$r = 4$ mm	$r = 12$ mm	General mean
314	295	273	
292	280	269	
282	303	273	
286	294	319	
299	322	276	
290	295	329	
	290	315	
Mean 297	294	293	295

First specimen, new series.			
$r = 1$ mm	$r = 4$ mm	$r = 12$ mm	
309	324	343	
304	306	301	
281			
316			
Mean 303	315	322	311

Second specimen.			
$r = 1$ mm	$r = 4$ mm	$r = 5$ mm	
286	279	332	
320	294	279	
334	303		
316			
Mean 314	292	306	305

Relation of penetration-hardness to elasticity

The indentation-hardness (H) and the modulus of penetration (E') (which is nearly the same as Young's modulus, see p. 437) are roughly proportional in quartz (two directions) and vitreous silica, as is evident from the following comparison:

	E'	H	$\frac{E'}{H}$
Quartz, force parallel to principal axis.....	1040	30.2	34
Quartz, force perpendicular to principal axis....	840	22.5	37
Vitreous silica	680	21.9	31

[48] Ann. Phys. u. Chem. (1896) **58**: 357-380.

By means of penetration-hardness measurements on 14 glasses, Auerbach [49] was able to assign a certain hardness-coefficient to each of the 10 oxide constituents of all but 2 of the glasses. Such coefficients had already been determined by other investigators for the tensile strength, compressive strength, refractive index, etc., of these same glasses. These coefficients are only approximate in character, for they take no account of the various modes of combination of the oxides in the glasses. It is therefore interesting to note that when the coefficient for silica is multiplied by 100 to give a kind of "extrapolated" hardness for pure silica, we obtain 32.5 kilomegabaryes, agreeing fairly well with the measured hardness of quartz on a basal plate (30.2) and lying about 50 per cent higher than the hardness of pure vitreous silica (21.9).

Dynamic hardness tests

The mineralogical scale of hardness

A crude and qualitative, but very useful and generally employed test, is that devised by Mohs. It consists in selecting a row of 10 standard substances each of which will scratch the surface of its neighbor to the left, while it can itself be scratched by its neighbor to the right. The standard substances are numbered 1 to 10, in their serial order. The unknown substance is then tested with these standards, and its hardness number is that of the standard which it can most nearly replace in the row.

Low-quartz is one of the standard substances in Mohs' scale of hardness, being assigned the number 7. Since no basis of interpolation is provided, there can be no such thing as a hardness of 6½ or 7.3, unless the scale be extended by the addition of other standards with assigned numbers.

Vitreous silica comes very near replacing quartz in the series, so must also be given the number 7.

Other kinds of hardness

The difficulties, both practical and theoretical, with a scale of hardness of the Mohs type were soon recognized. Efforts to improve upon his scale followed two principal directions:

(A) Attempts to define quantitative and reproducible conditions under which to make a scratch on the surface of the substance tested.

(B) Attempts to define quantitative and reproducible conditions under which the surface of the substance tested may be abraded away by a powder of some other substance.

Table XXIV.8 gives a general summary of the comparative hardnesses of corundum and quartz, as tested by some of the various scratching and abrading methods that have been proposed.

[49] Auerbach, F., Ann. Phys. u. Chem. (1894) 53: 1000-1038.

Measured scratch-hardness

The numerous experiments on hardness from which the data in Table XXIV.8 are quoted have brought out clearly the fact that scratch-hardness depends not only upon the composition of the substance but also upon (a) the crystal plane upon which the test is made; (b) the direction of the scratch. This is naturally to be expected, because the manner of arrangement of atoms along any direction or in any plane of the crystal is in general different from that in other directions or planes.

In a given plane of any crystal the scratch-hardness may be expected to be greatest in the direction perpendicular to the trace of a cleavage plane, and least in the direction parallel thereto. This is not an important criterion in quartz, which has hardly any recognizable cleavage. The scratch-hardness parallel to the principal axis, however, is considerably greater than that perpendicular to the axis, on any face on which both are measurable.

TABLE XXIV.8.

RELATIVE SCRATCH-HARDNESS AND ABRASION-HARDNESS OF QUARTZ COMPARED WITH CORUNDUM, BY VARIOUS METHODS.

Author	Method	Corundum	Quartz
Mohs (1822)	Series of 10 minerals arranged in serial order, from diamond (10) to talc (1).	9	7
Franz (1850)	Load measured which produces scratch.	1000	667
Martens (Berndt, 1919).	Diamond with 90° conical point; H = load required to make a scratch 0.01 mm wide.		73, direction ∥ to axis 59, direction ⊥ to axis
Pfaff (1883)	Movable arm, diamond chisel; H = reciprocal of volume cut away.		266, plane {0001} 536, plane {10$\bar{1}$0}
Pfaff (1884)	Revolving diamond; H = number of revolutions required to reach given depth.	1000 *	390, plane {0001} 530, plane {10$\bar{1}$0}
Rosiwal (1896)	H = reciprocal of volume lost by grinding with emery.	1000 †	175, average 222, plane {0001} 189, plane {10$\bar{1}$0} 181, rhombohedron
Rosiwal (1896)	H = reciprocal of weight lost by grinding with emery.	1000 †	117, average 149, plane {0001} 127, plane {10$\bar{1}$0} 122, rhombohedron

* Best cleavage-face.
† Average of several faces.

The measurements of scratch-hardness of quartz by the Martens apparatus, quoted in Table XXIV.8, were made by Berndt,[50] who gives the values 73.3 parallel to the axis and 59.4 perpendicular thereto. These figures are the "average of a rather large series of experiments" but it is not stated whether the tests were made on natural faces or on polished plates.

Abrasion-hardness

The abrasion test for hardness has been extensively studied by Holmquist,[51] who has shown that the size of grain of the abrasive powder is the most important factor in the test. An abrasion test in which the average size and the distribution of sizes of the abrasive is not known or controlled is therefore of little value.

This change of abrasion-hardness with size of the abrasive is shown in Table XXIV.9, which compares quartz with topaz, its next higher neighbor on the Mohs scale. It is seen that the relative order of hardness of the two actually reverses with changing size of the abrasive. In these tests the numerical hardness is taken as proportional to the thickness of material abraded away from the surface, when plates of the two substances are ground for a short time one against the other, with an abundance of powdered abrasive of known size of grain between them.

TABLE XXIV.9.

RELATIVE ABRASION-HARDNESS OF QUARTZ (BASAL PLANE {0001}) AND TOPAZ (PLANE PERPENDICULAR TO {001}). HOLMQUIST, 1922.

Basis: Quartz, plane {0001}, hardness = 1000.

Size of carborundum abrasive μ	Number of tests	Abrasion-hardness of topaz
2 to 5	11	1246
5 to 10	7	1180
10 to 20	5	943
30 to 40	3	923
40 to 50	4	880

According to the experience of the Japanese quartz workers, the prism faces of a quartz crystal are the hardest, that is, the most resistant to cutting and grinding. The artificial basal plane (plane perpendicular to the axis) is much softer than the natural crystal faces.[52]

In view of the experiments by Holmquist, not much weight can be given the comparison by Jannetaz & Goldberg,[53] who ground three different planes on quartz in their "usometer" and compared the losses of weight. The relative losses were:

Plate perpendicular to axis	1
Plate parallel to axis	1.09 to 1.19
Plate parallel to rhombohedron	1.26 to 1.32

[50] Second article cited in note [26].
[51] HOLMQUIST, P. J., Geol. För. Förh. (1922) **44**: 485-504.
[52] ICHIKAWA, S., article cited in XXV, note [19].
[53] JANNETAZ, P., & GOLDBERG, M., Assoc. Franc. Av. Sci. (1895) **II**: 417-425.

The relation of parallel to perpendicular surfaces is the opposite of that found by Pfaff [54] and by the Japanese, but similar to that found by Rosiwal.[55]

Comparative scratch-hardness of quartz and vitreous silica

H. Rose [56] recognized in 1859 that quartz is of nearly the same hardness as vitreous silica and some specimens of opal. Heraeus [57] gives the hardness of vitreous silica as "between feldspar and quartz," which means that it is not as hard as quartz.

Shenstone & Lacell [58] report observations by Pentecost that the glass is less hard than chalcedony but harder than feldspar. He noticed also that its surface was equally hard whether it had been heated as hot as possible in the oxy-gas flame and then chilled, or whether it had been heated and cooled at its natural rate in air.

The hardnesses of low-quartz and an impure vitreous silica have been compared by Johns & Desch.[59] With 400 grams on the diamond point of a sclerometer a broader scratch was made on a prism face of quartz than on a polished surface of the glass. Qualitative tests showed that fractured edges of the glass would scratch the prism faces of quartz, while the natural angles of the quartz failed to scratch the glass. The tests indicated that the glass was a little the harder. But both of the sclerometer scratches were splintery, and, furthermore, the glass contained about 2.0 per cent CaO and a trace of iron, with only 97.7 SiO_2, having been made by throwing quartz sand on to a surface of open-hearth slag at about 1800°C. It is therefore too impure to furnish a really satisfactory comparison.

Scleroscope (rebounding hammer) tests were also made by Johns & Desch, with the following results:

Polished translucent vitreous silica, 97.7% SiO_2	94
Commercial vitreous silica	82
Prism face of quartz	91

Not much reliance can be placed upon the test of the scratching of one fragment by another. The simple test of scratchability does not meet one of the fundamental requirements of a quantitative measure, namely, that if A is greater than B then B is less than A; for, as Auerbach [60] was able to show, in a series of glasses of very different hardness each was capable of scratching all the others. The results are more dependable when the scratches are examined microscopically to judge which of a pair has scratched the other the deeper, but even then the order of hardness is not wholly consistent from different sets of pairs.

[54] Pfaff, F., Sitzungsb. Bayer. Akad. Wiss. München, M.-P. Cl. (1883) 55, 372; (1884) 255.
[55] Rosiwal, A., Verh. K. K. Geol. Reichsanst. Wien **1896**: 475-491.
[56] Article cited in IV, note [12].
[57] Article cited in V, note [18].
[58] Nature (1900) **62**: 20-22.
[59] Johns, C., & Desch, C. H., Nature (1923) **111**: 15.
[60] Article cited in note [49].

Chapter XXV. SURFACE ENERGY

The properties of silica considered in the preceding chapters have been, for the most part, properties of matter in the interior of crystals or fragments, with little reference to whether the portion of matter considered was near to or far from a bounding surface. Where finely subdivided silica was considered, it was usually with reference to the changed energy content of the material as a whole, resulting from the act of subdivision.

We must now take into account the fact that every portion of matter has a limiting surface which separates it from other portions of matter, and which causes the conditions surrounding any given atom in or near the surface to be different from the conditions in the interior of the fragment. The important group of facts relating to these limiting surfaces are brought together in this chapter, which might have been given the heading "inter-phase properties."

Crystal habit

A knowledge of the positions in space of the atoms of a substance is not sufficient, in the present state of physico-chemical science, to enable us to predict what faces it will develop if it occurs in euhedral (good-faced) form. The symmetry of the substance is of course the same, whether it occurs as random irregular lumps of no characteristic external shape or whether it forms the most perfect geometrical figures. Its external shape is wholly a matter of bounding surfaces and is thus properly considered as an inter-phase property.

Crystalline faces usually result from the growth of the crystal out of a melt or solution. The shape of euhedral material therefore depends upon two things: (1) what faces are physically capable of occurrence, and (2) how the faces grow relatively to one another. For example, a substance of hexagonal symmetry may be capable of growing as six-sided prisms with plane ends. Its characteristic faces are then the *base* and the *hexagonal prism*. But this is not the whole story. It may grow very rapidly in the direction of the three equatorial axes but hardly at all in the direction of the principal axis, and may thus form thin hexagonal plates; or it may grow very rapidly along the principal axis and very slowly along the equatorial axes and thus form long needles.

Thus it happens that nearly every substance, when in euhedral form, shows characteristic groups of faces which develop into characteristic external shapes or *growth-forms*, such as plates, prisms, needles, and the like. These shapes are referred to as the *habit* of the crystalline substance under the conditions described. The habit may, and often does, vary with the conditions of growth, such as temperature, impurities in the solvent, and other variables whose effect is as yet little understood.

The geometrical forms assumed by crystalline substances made up the greater part of the foundation material of crystallography and mineralogy in the early days of those branches of science. Hence the mineralogic and crystallographic reference books have always contained abundant detail on crystal habit, and there is no need to devote much space to it here, at least so far as the natural silica minerals are concerned.

The standard tables for reference are V. Goldschmidt's tables [1] and his monumental atlas [2]. Full lists of crystal-forms are also given by Dana and Hintze in their mineralogies.

TABLE XXV.1.

COMMONEST CRYSTAL-FORMS OF LOW-QUARTZ.

Indices	Usual symbol	Descriptive name
$10\bar{1}1$	r	Primary positive rhombohedron
$01\bar{1}1$	z or r'	Primary negative rhombohedron
$10\bar{1}0$	m	Hexagonal prism (first order)
$51\bar{6}1$	x	Common right positive trapezohedron
$6\bar{1}51$	x	Common left positive trapezohedron
$11\bar{2}1$	s	Common right trigonal pyramid
$2\bar{1}11$	s	Common left trigonal pyramid

A geometrical crystal-form consists of a set of crystal faces all of which bear a similar relation to the elements of symmetry of the substance (see XII). For example, the 6 faces of the hexagonal prism constitute a form, and the two basal planes constitute another form. An hexagonal prismatic crystal is bounded by a combination of the two. This is a very different use of the word "form" from that introduced in Chapter IV, where reference is frequently made to the "forms of silica," but the two meanings are so entirely distinct that no confusion seems likely to occur.

Crystal habit of the modifications of silica

The following list gives the prevailing habit of the better-known modifications of silica:

Modification	Habit
Low-quartz	Prismatic
High-quartz	Pyramidal (hexagonal pyramids)
Low-tridymite	(Not known in euhedral development)
Lower high-tridymite	(Not known in euhedral development)
Upper high-tridymite	Tabular (hexagonal plates)
Low-cristobalite	(Not known in euhedral development)
High-cristobalite	Octahedral. Skeletons

[1] GOLDSCHMIDT, V., *Krystallographische Winkeltabellen* (1897, Berlin) pp. 288 and 419 (quartz), 349 (tridymite).

[2] GOLDSCHMIDT, V., *Atlas der Krystallformen* (1913-1923, Heidelberg). Quartz in Vol. 7, pp. 60-108, atlas pls. 54-108; tridymite in Vol. 9, pp. 2-4, atlas pls. 1-4; cristobalite in Vol. 2, p. 195, atlas pl. 247.

Low-quartz

The crystal-forms most commonly found on low-quartz are listed in Table XXV.1. The first column gives the Miller-Bravais indices of the form. The second column gives the designation of the faces commonly used in illustrations and descriptions; these letters have no relation to one another and are purely arbitrary "markers," like the number on a hat in a check-room. The third column contains the usual name of the form.

Taking the 7 most common crystal-forms, namely, *m, r, z, s* right, *s* left, *x* right, and *x* left and allowing for the fact that right and left forms can not occur on the same homogeneous unit, it is possible to calculate the number of varieties of crystal shapes which quartz may assume through the combination of these different forms. The form-combinations are:

Number of forms combined	Number of possible combinations
1	6
2	17
3	19
4	9
5	2
6	0
7	0
Total	53

Each of the form-combinations, further, may give rise to a series of actual shapes, depending upon which form predominates over the others.

When we add the less common crystal-forms, the number of possible shapes of low-quartz runs into the thousands. Euhedral quartz is fairly common and abundant, hence the assembling of as many as possible of these combinations would make a capital pastime for anyone who has the collecting instinct; and not a wholly idle pastime, either, for the frequency or the absolute non-occurrence of certain combinations will furnish information concerning both the structure of quartz and the conditions of its formation in nature.

Single forms of low-quartz

Either rhombohedron may occur alone, giving the calcite-shaped rhomb shown in Figures XII.4 and 5. Quartz is very rarely found in this habit. The hexagonal prism cannot occur alone, as it is not a "closed form," and the pyramids and trapezohedrons have never been found to occur alone.

Combinations of two crystal-forms

The prism faces are entirely lacking on some quartz crystals, and only the positive and negative primary rhombohedrons are present. This kind of development gives a *birhombohedral* crystal, looking like a double hexagonal pyramid when the two rhombohedrons are equally developed, when it is often called a *quartzoid.*

The external symmetry of crystals of such shapes is normal hexagonal (dihexagonal bipyramidal class) and the true symmetry of low-quartz is concealed. Usually, however, the positive rhombohedron predominates in size.

Combinations of three or more crystal-forms

The commonest combination of 3 crystal forms is that of the prism with the two primary rhombohedrons. The latter are sometimes equally developed, again giving a crystal of normal hexagonal symmetry, but repression of the negative rhombohedron is the more usual case (see Fig. XII.6).

Horizontal striations on the prism faces are very common, and are a useful aid to the crystallographer in placing the axes of a crystal whose forms are indistinct. The striations are due to the repeated starting and stopping of rhombohedral faces during the growth.

A familiar five-form combination is that of the prism and two rhombohedrons, with corners truncated by the trapezohedron x and the pyramid s. This is the standard low-quartz crystal for the illustration of physical properties (see Fig. XII.7 or Fig. XXIII.8).

The data on the habit of low-quartz

Experimental data

Low-quartz crystals as prepared in the laboratory are usually bounded by the group of seven most common forms just described. Some of them are very perfect, being doubly terminated, with the hexagonal prism and rhombohedrons as bounding faces. Unfortunately it happens too often that detailed data on the habit of such crystals are not recorded by the investigators who prepare them.

A few typical descriptions are assembled in Table XXV.2.

Table XXV.2.
Experimental Data on the Habit of Low-Quartz.

Observer	Temp. of preparation	Habit
Schafhäutl (1845)	Not stated	Hex. prism and pyramid [rhombohedrons]
Chrustschoff (1887)	250	{10$\bar{1}$0}, {10$\bar{1}$1} predominant; {01$\bar{1}$1}, {11$\bar{2}$1} rare
Bruhns (1889)	300	{10$\bar{1}$0}, 2 rhombohedrons, one predominating
Daubrée (1857)	320	{10$\bar{1}$0}, {10$\bar{1}$1}, {01$\bar{1}$1}, and trapezohedron
Koenigsberger & Müller (1906)	360	{10$\bar{1}$0}, 1 rhombohedron well developed, 1 rare and small
Day, Shepherd & Wright (1906)	400 to 450	{10$\bar{1}$0}, {10$\bar{1}$1}, {01$\bar{1}$1}, {11$\bar{2}$0} Short rhombohedrons passing by oscillatory development into steeper rhombohedrons and prism. Horiz. striae on prism

Observational data on the habit of quartz

Goldschmidt lists no fewer than 123 crystal-forms of quartz, all of which have been observed on natural crystals.

Since the conditions of growth of most of these crystals are unknown, there is no means of discriminating between the habit of high-quartz and that of low-quartz in this collection of crystal-forms. Let us suppose that one of the natural crystals in Goldschmidt's collection grew out of a solution at temperatures above 573°C. Under these conditions it may have possessed a certain characteristic crystal-form which low-quartz grown below 573° would never have shown. Nevertheless the low-quartz crystal which was produced from this high-quartz by inversion was compelled to inherit the bounding planes of the high-quartz, and this particular crystal-form is therefore listed among the 123.

To be sure, it is probable that most of the euhedral quartz found in nature has grown at temperatures well below 573°, and we can therefore make the general statement that most of Goldschmidt's 123 forms probably belong to low-quartz, but this does not tell us which forms to eliminate.

There are in the published records many data on the habit of natural quartz in association with rocks which are assumed to have been above 573° when the quartz crystallized, and these observations might be supposed useful as a basis for selecting the forms characteristic of high-quartz. But the reasons for the assumed temperature are usually not very strong, and the line of argument, furthermore, has no logical validity unless the observer has seen the quartz crystallizing and knows by measurements of temperature that the magma was above 573° at the time. It might seem unnecessary to insist upon this point, were it not for the fact that the petrologists have been trying in recent years to use quartz as a "geologic thermometer" and to deduce its temperature of formation from its observed properties. Now it is obviously bad science to proceed by first assuming a temperature and then using the properties deduced therefrom to prove that the temperature had the value assumed. The only safe course is to set aside for later use all the petrologic data on the habit of quartz, and hold strictly to the experimental data.

The most thorough and exhaustive observational research on the habit and twinning of quartz is that of Des Cloiseaux.[3] It furnishes the groundwork for all subsequent studies of the crystal-forms of quartz, and is fittingly described by Senarmont[4] as "one of the most complete monographic studies that has ever been made on a mineral species." Des Cloiseaux was led into this work through the examination of specimens from a locality in France, on which he found several new crystal-forms. He then extended the work to include all available specimens in the public and private mineral collections in Paris, and also obtained many specimens from other countries for comparison.

The most important contribution preceding that of Des Cloiseaux is the paper of Rose.[5] He measured and described quartz crystals from 12 locali-

[3] Des Cloiseaux, *Mémoire sur la cristallisation et la structure intérieure du quartz*, Ann. Chim. et Phys. (1855) (3) **45**: 129-316.

[4] Senarmont, Compt. rend. Acad. Paris (1855) **40**: 1132-1138.

[5] Rose, G., *Über das Krystallisationssystem des Quarzes*, Physik. Abhandl. Akad. Wiss. Berlin 1844: 217-274.

ties, bringing out clearly their relations in symmetry and habit, and illustrated the discussion with 51 engraved figures.

At present all of this material, and much else of the same kind but in more scattered form, stands as purely descriptive and classificatory. Its further meaning can only be brought out through the correlation of habit with conditions of growth, by means of laboratory experiments.

Twinning habits of quartz

The general geometry of the twinning of quartz and of tridymite has already been discussed in the chapter on symmetry (XII). Some further details are now in order, as to how the geometrical principles are actually applied in natural and artificial crystals.

The logically simplest form of a twin is one in which the two parts are equally developed and are united along the composition plane. Actual twins are seldom so perfect as this. The two parts are likely to be unequally developed, and the surface of junction is not necessarily the composition plane, for the two parts may be joined along a somewhat irregular surface. Nevertheless the two are in many cases distinct enough to be roughly separable by a saw cut, and the twin is then called a "juxtaposition twin" or *contact twin*.

This habit grades over gradually into a condition of intermingling of the two parts. Twins of this habit are called *penetration twins* and are very common in quartz, in both Dauphiné and Brazil twins.

Another habit of twinning is that in which there is a series of unit crystals of which any two neighboring units are in twinning relationship. This is called *repeated twinning*.

If the units are all in parallel alternating position, the habit is called *polysynthetic twinning*. This habit is characteristic of amethystine quartz

Repeated twinning

Low-quartz is one of the substances that show repeated twinning, consisting of the alternate repetition of equal or nearly equal thicknesses of the two varieties.

The commonest type is repeated lamellar chiral (Brazil) twinning, with the planes of the lamination parallel to the trigonal prism. A section perdendicular to the axis, seen in polarized light, may then show a series of concentric hexagons, or patterns equivalent thereto if the fragment as a whole is not symmetrically constructed.

This chiral lamellar twinning is often developed in conjunction with the violet coloration characteristic of amethyst. The violet-colored and lamellar portions of a composite fragment are sometimes found arranged in alternate 60-degree sectors of the cross-section.

Polysynthetic twinning of the chiral type in quartz sometimes becomes very intricate, with the positive rhombohedron as composition face, so that

he resulting crystal consists of alternating fine lamellae of right- and left-quartz. Such an aggregate has the symmetry of a ditrigonal-scalenohedral (class 21) crystal such as calcite, and shows no optical rotatory power.

A special type of repeated Dauphiné-twinned quartz is the so-called "twisted" (German *gewunden*) crystal. A large number of individuals (all right or all left) are combined almost parallel to one another along a horizontal axis, but the vertical axes deviate from one another by successive small and equal amounts, with the result that the aggregate has helically wound surfaces.

Experimental data

There are few direct observations on experimentally-grown quartz which could be used to show any correlation between temperature of formation and character of twinning.

Experience with the crystallization of other substances indicates that a homogeneous one-way crystal of quartz is more likely to form from a melt or solution which is crystallizing in place than from a melt or solution which is being renewed constantly. In the undisturbed melt or solution the nuclei first formed are built upon continuously, giving an untwinned crystal. But if the source of supply is being continuously or frequently renewed, fresh nuclei may start, or the conditions may vary so as to favor first right-handed and then left-handed growth.

The crystals grown under the first-mentioned conditions, if grown above 573°, may still not remain untwinned, for Dauphiné twinning is known to be produced by the inversion on cooling through 573°. But right-and-left twinning is not known to be produced in this way.

Inference from the known relations of properties to temperature is in favor of the belief that when quartz crystallizes it always does so with the kind and degree of optical rotatory power which we afterwards find in it. As just noted, Brazil twinning has never been observed as a result of heating and cooling. Furthermore, natural quartz when heated retains its rotatory power with unchanged sign up to the highest temperature at which observations have been made (about 1500°). This temperature is far above the stability-range of quartz, in a region of temperature where quartz has never been known to form from a melt or solution. It is reasonable to suppose, then, that when quartz crystallizes below 870°, within its stability-range, it separates as an optically rotatory crystal, and never as an optically inactive mixed-crystal which later separates into right- and left-handed modifications.

DATA ON HIGH-QUARTZ

Since the symmetry class of high-quartz differs from that of low-quartz, we may expect that crystals grown at a temperature above 573° will have a characteristic habit different from that of low-quartz. This is found to be the case.

The commonest crystal-forms of high-quartz are the first-order hexagonal bipyramids $\{10\bar{1}1\}$ and $\{20\bar{2}1\}$. The first-order hexagonal prism $\{10\bar{1}0\}$ also occurs, but much less commonly than in low-quartz.

Typical observations are given in Table XXV.3.

TABLE XXV.3.

EXPERIMENTAL DATA ON THE HABIT OF HIGH-QUARTZ.

Observer	Temp. of formation	Habit
Hautefeuille (1878)	750 to 850	{20$\bar{2}$1} best. Spindle-shaped, from extension of sharp pyramids.
Hautefeuille (1878)	750 to 850	{40$\bar{4}$1}, {10$\bar{1}$0}.
	Below 800	{10$\bar{1}$1} frequent. More faces than above 800°.
	Above 800	{20$\bar{2}$1} best.
Hautefeuille & Margottet (1881)...	Below 960	{10$\bar{1}$0} and pyramid, no modifying facets.
Hautefeuille (1880)	Below 1000	{10$\bar{1}$0} and {10$\bar{1}$1}. Marked channels on prism faces.

TRIDYMITE

There are no specimens of tridymite which are known to have been formed from a solution or melt at temperatures below 117° or even below 163°. Hence the habit of growth of low-tridymite and of lower high-tridymite is unknown.

When produced by inversion from the high-modifications, low-tridymite usually forms an aggregate of twinned individuals, the aggregate as a whole inheriting the external shape of the upper high-modification.

Habit of the high-tridymites

Natural tridymite always shows evidence of having passed through an inversion temperature. The doubt that exists as to whether any given specimen of natural quartz was formed below or above 573° therefore does not apply to tridymite; it has always been formed *above* 117°. A second uncertainty now enters, however, for we have no means of knowing whether a given specimen formed between 117 and 163° or whether it formed above 163°. In this case, however, it is reassuring to note that the upper high and lower high modifications differ very little in properties, and we shall therefore not be far from the truth in assuming that the observed habit of natural tridymite is characteristic of both of the high-modifications.

The commonest growth-form of natural high-tridymite is an hexagonal plate, bounded by prism faces perpendicular to the plate. The prism edges are sometimes truncated by a dihexagonal prism; and the plate edges by the unit hexagonal pyramid.

The commonest forms and their usual designations are given in Table XXV.4.

TABLE XXV.4.
CRYSTAL-FORMS FOUND ON HIGH-TRIDYMITE.

Indices	Symbol	Name
{0001}	*c*	Base
{10$\bar{1}$0}	*m*	Hexagonal prism
{54$\bar{9}$0}	*l*	A dihexagonal prism
{10$\bar{1}$1}	*p*	Hexagonal pyramid

In artificial preparations tridymite is commonly found in the form of cryptocrystalline aggregates of hexagonal habit, and also as perfectly formed hexagonal plates. Interpenetration twinning is common. The crystals in many random aggregates show elongated or lath-like shapes, due to their being cross-sections of thin plates. In other cases a characteristic wedge-like twinning occurs.

A characteristic quality of tridymite is its habit of growing in groups of three twinned individuals, or "trillings." This is the origin of the name of the mineral (see p. 42).

Lacroix[6] concluded from his study of tridymite in siliceous inclusions and in cavities that tridymite of pneumatolytic origin is characterized by a habit of growth in very thin hexagonal plates intricately intergrown, while tridymite formed in melts is in flat prisms or thick hexagonal plates, twinned in the usual manner. Le Chatelier's observation[7] of very thin tridymite, sometimes grouped in spherulites, in a partly devitrified lead glass, led Lacroix[8] to modify his view and to recognize that the thin and intergrown plates may also be representative of growth from melts and need not be of pneumatolytic origin alone.

HABIT OF CRISTOBALITE

As with tridymite, we cannot claim to know anything at all about the habit of growth of low-cristobalite, because all the low-cristobalite which has ever been examined crystallographically has been the product of the inversion of high-cristobalite. The result is always an aggregate of very small units of the low-modification, whose individual properties are difficult to determine.

High-cristobalite

The prevailing habit of growth of high-cristobalite in natural occurrences and in many artificial melts is octahedral; cube faces are less common. In certain silicate melts, however, cubic forms are the more usual.

Perhaps the most striking feature about its habit is its production of

[6] LACROIX, A., Bull. Soc. Franc. Min. (1908) **31**: 323-338.
[7] Article cited in IV, note [22].
[8] LACROIX, A., Same (1916) **39**: 154-155.

skeletons, the octahedral corners being developed perfectly with intermediate edges and faces incomplete, or the corners and edges being both developed but with the intervening faces hollow and incomplete. The excessive development of octahedral angles is especially conspicuous in the twins.

Twinning of the spinel type is common in high-cristobalite (see XII). As observed in vom Rath's original specimens, it gave the crystals the form of three-sided plates. It leads to angles of 45 and 60 degrees between the branches of the skeleton crystals.[9]

The experimental and observational data on cristobalite

Our knowledge of the habit of high-cristobalite is drawn almost entirely from observations on the fine-grained aggregate of low-cristobalite which results from the inversion of the high-modification.

Vom Rath, discoverer of cristobalite, noted its skeletal development in his original specimens (p. 58).

Mallard[10] was able to get fairly good measurements from the faintly reflecting faces of octahedral aggregates from the original locality, and found 70° 21′, almost identical with the angle of the geometrical regular octahedron.

Holmquist[11] observed well-defined octahedrons of cristobalite in partly fused silica brick taken from a steel-melting furnace. Usually, however, the grains had irregular and rounded contours. The best developed crystals were in those parts of the mass where a silicate glass, formed by the lime and the impurities, was abundant. In places where quartz had been converted into cristobalite without transport of material, the cristobalite was extremely fine-grained and interstitial glass was nearly absent.

A characteristic feature noted by Holmquist in the cristobalite (and also tridymite) derived from quartz is the presence of spheroidal (perlitic) fractures throughout the mass. In some places these become partings which are more or less plane, following the contours of cristobalite grains, and either roughly perpendicular or at about 70° to one another. It seems probable that these partings are approximations to cleavages parallel to the forms {100} and {110}, respectively, of high-cristobalite.

In artificial preparations cristobalite very commonly occurs in cryptocrystalline aggregates, but can be made to grow into recognizable forms.

Cristobalite crystals large enough for microscopic study (0.1 to 0.2 mm) can be obtained by heating amorphous silica with fused sodium tungstate. These crystals are usually irregular branching sketetons, with terminal octahedral caps. The direction of elongation of the branches is along cubic axes.[12]

In many silicate melts cristobalite can be seen to have retained the crystal outlines of the isotropic high-modification. When embedded in glass the crystals are sometimes sharply outlined octahedra, modified by the cube. In most melts the cube is the more prominent form and the crystals are, by

[9] Fenner, article cited in IV, note [2].
[10] Article cited in IV, note [18].
[11] Article cited in V, note [9].
[12] Fenner, C. N., articles cited in IV, note [2].

distortion, stout prisms produced by slight elongation parallel to one of the cube axes. Occasional polysynthetic twinning has been observed.[13]

Le Chatelier (see note [7]) has described cristobalite formed by the devitrification of aluminous lead glass (*quinquet*) in which it grew as irregular spherulites 1 to 3 mm in diameter.

In the type occurrence of vom Rath, cristobalite forms small white crystals, most of which are nearly opaque and without polish on the faces. Some few have a partial polish and are somewhat translucent. They are all fairly translucent when immersed in a liquid.

Most of them are badly formed or without any crystalline form. They have the shape of arrows with rounded edges and enlarged at the middle. Where octahedral crystals show they are formed by the production of a four-faced point on the arrow; the plane of the arrow and that of its two axial enlargements form the two diagonal planes of the point. The octahedral faces are not always complete and some of the crystals are hollow. The crystal sometimes covers and envelops a point of the rock.

Further data on the habit of cristobalite will be found in papers by Rogers,[14] Shannon,[15] Foshag,[16] and Weil.[17]

Geometrical anomalies in silica

Under certain conditions the crystals of many substances fail to develop the complete symmetry of faces called for by their class. They seem to fall into a class of lower symmetry. Such vagaries are called *geometrical anomalies*. Some examples of this phenomenon in silica are given below.

Quartz

Quartz crystals from Dauphiné are found with only three prism faces instead of six. Quartz crystals from Striegau (Silesia) show hexagonal prism faces which are clearly classifiable into two groups of three each, differing in the kind of striations on the faces.

Tridymite

Some tridymite crystals show a horizontal line across the prism faces. This can be interpreted as a tendency toward hemimorphism with respect to the principal axis, accompanied by twinning with the base as twinning plane.

Etch-figures and solution-forms

The next set of inter-phase properties to be discussed is the inverse of that just considered. The rate and manner in which a crystal grows

[13] Bowen, N. L., & Andersen, O., Amer. J. Sci. (1914) **37**: 487-500.
[14] Rogers, A. F., Amer. J. Sci. (1918) **45**: 222-226; Journ. Geol. (1922) **30**: 211-216.
[15] Shannon, E. V., J. Wash. Acad. Sci. (1922) **12**: 195-196; Proc. U. S. Natl. Mus. (1923) **62**: art. 12.
[16] Foshag, W. F., Proc. U. S. Natl. Mus. (1926) **68**: art. 17.
[17] Weil, R., Compt. rend. Acad. Paris (1925) **181**: 423-425.

determine its crystalline habit and its growth-forms. The rate and manner in which it dissolves are expressed in its *etch-figures* and *solution-forms.*

Etch-figures are very small angular pits or hummocks formed in or on a previously smooth surface of a crystal by the action of a solvent. A solution-form is the shape approached by a fragment of the substance when a considerable fraction of it has been dissolved away.

Like the growth-properties, these dissolving-properties vary with external conditions such as the temperature, the composition, and the concentration of the solvent, but they usually (not always) remain expressive of the accepted symmetry of the substance.

Practically all of the work of this character on silica has been on quartz. The principal solvents used have been aqueous hydrofluoric acid, and water solutions of the alkali hydroxides or carbonates.

Natural etching, perhaps by alkaline waters, has also been the subject of occasional observations.

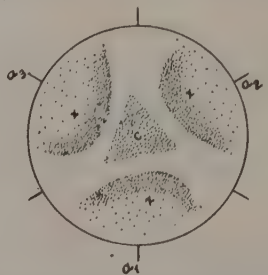


FIG. XXV.1.—Sketch to show character of etching of a sphere of right-low-quartz by hydrofluoric acid. Polar view. Nacken, 1916.

LOW-QUARTZ

The etch-figures produced on low-quartz by hydrofluoric acid are quite different from those produced by solutions of alkali hydroxides or carbonates, but in practically all cases the form and position of the etch-figures are in agreement with trigonal trapezohedral symmetry.

Dilute hydrofluoric acid acts first upon the rhombohedrons without attacking other faces. Of the two rhombohedrons, the negative, *z*, is the more rapidly attacked, becoming mat in appearance because of the great number of small pits, while on the positive, *r*, there are fewer and larger pits.

Of all the simpler planes of low-quartz the plane {0001}, perpendicular to the axis, shows the greatest diversity in etch-figures. The etch-figures with HF are particularly variable. Etch-hills in place of etch-pits are the usual form on this plane.[18]

[18] BÖMER, A., Neues Jahrb. Mineral. (1891) Beil.-Bd. 7: 516-555.

The grooves etched at the edges of a quartz crystal are also of interest. In strong hydrofluoric acid a groove is formed along each of the 3 positive edges of the prism. In crystals etched in nature, presumably by alkaline solutions, only the 3 negative edges are grooved. Edges between two positive or two negative rhombohedrons are grooved by hydrofluoric acid, and are also found grooved by natural etching.[19]

Solution-forms

A sphere of quartz placed in aqueous hydrofluoric acid is attacked at very different rates along different radii. As the material dissolves away the sphere therefore gradually loses its original form and is converted into a solid having trigonal trapezohedral symmetry.

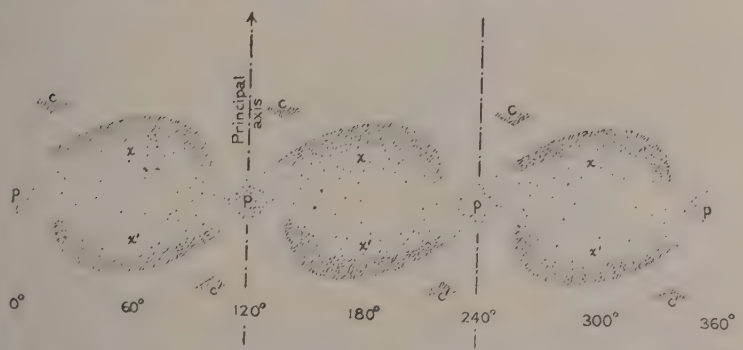


FIG. XXV.2.—Sketch to show character of etching of a sphere of right-low-quartz by hydrofluoric acid. Development of equatorial view. Nacken, 1916.

THE EXPERIMENTAL DATA ON ETCHING AND SOLUTION OF LOW-QUARTZ

Our knowledge of etch-figures on low-quartz comes principally from the experiments of Molengraaf (1888), Meyer & Penfield (1889), Bömer (1891), Gill (1894), Spezia (1898 to 1909), Mügge (1906), Ichikawa (1915), Lincio (1916), and Nacken (1916).

Since no principles of general application have resulted from the experiments, the results will not be considered in detail. We may expect, however, that a clearer understanding of the phenomena of production of these variable and sometimes very complex etch-figures will soon be brought about with the aid of the new knowledge of structure obtained with the X-rays.

The most extended recent studies on low-temperature etching, both artificial and natural, are by Ichikawa.[20] His experiments on crystals, plates, and spheres

[19] ICHIKAWA, S., *Studies on the etched figures of Japanese quartz*, Amer. J. Sci. (1915) 39: 455-473.

[20] Article just cited, also various articles in Japanese.

have supplemented Molengraaf[21] and Meyer & Penfield[22] by showing the results obtained at successive stages of the action of hydrofluoric acid.

A good example of the symmetry of distribution of the etch-figures is found in Nacken's experiments[23] in etching a sphere of low-right-quartz at 30°C with a mixture of 10 parts aqueous hydrofluoric acid and 1 part concentrated sulfuric acid. The distribution of the resulting etch-figures is shown in the sketches, Figures XXV.1 and 2. Figure XXV.1 shows a polar view of the sphere as brought out by blackening the etch-pits with graphite, and Figure XXV.2 is the complete equatorial view. The field *c* corresponds to a

FIG. XXV.3.—Curve illustrating the rate of dissolution of surfaces of quartz normal to directions making various angles with the principal axis. Mügge, 1906.

basal plane, *p* to a trigonal prism, and *x* to a trapezohedron. A measurement of the light-figures obtained by passing a beam of light through the etched sphere set in Canada balsam under the microscope shows that the principal refracting surface in the field *x* is the trapezohedron $\{51\bar{6}1\}$. The field *c'* at the opposite pole of the sphere is similar to the first, but the upper is rotated 20 to 30° to the right of the lower. The pits are equilateral triangular pyramidal, with sides turned 30 to 40° to the sides of the field as a whole.

The character of the solution-forms is well brought out by Mügge's extensive series[24] of measurements on the rate at which different planes of quartz dissolve in hydrofluoric acid. The rate was measured in terms of the loss of

[21] MOLENGRAAF, G. A. F., Zeitschr. Kryst. (1888) **14**: 173-201; (1889) **17**: 137-176.
[22] MEYER, O., & PENFIELD, S. L., Trans. Connecticut Acad. Sci. (1889) **8**: 158-165.
[23] Article cited in XII, note [8].
[24] MÜGGE, O., *Rosenbusch Festschrift* (1906, Stuttgart): 96-126.

weight of thin plates etched for a definite time in unstirred concentrated acid (40 per cent HF) at 20°C, and was expressed as mg per 1000 sq. mm per minute. The rate for different planes ranges from 0.46 for the basal plane to 0.003 for the hexagonal prism, a range of over 100-fold.

Similar results, though not so numerous or detailed, were obtained by Gill [25] from the change in shape of a sphere of quartz.

If the rate for each plane is plotted from a common center along a radius normal to the plane, a figure is obtained which shows graphically the change of rate with direction. A cross-section of this figure made by the plane $(1\bar{2}10)$, perpendicular to the positive rhombohedron and base, is shown in Figure XXV.3. The figure brings out well, by the character of its symmetry, the difference in rate between the positive and negative rhombohedrons.

The approximate change in shape of a dissolving sphere of quartz can be deduced from these data. Figure XXV.4 is a section of such a sphere by the

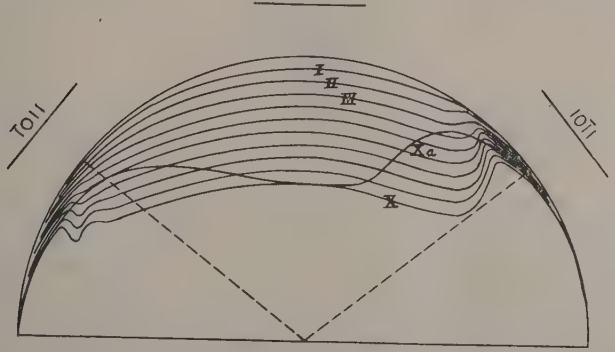


FIG. XXV.4.—Change of form of a sphere of quartz while dissolving, as deduced from the rates of dissolution represented in Figure XXV.3. Mügge, 1906.

plane $\{1\bar{2}10\}$ showing the forms attained at successive equal intervals of time, as deduced by measuring off distances proportional to the rate of dissolving in directions normal to each tangent plane of the surface. The curve X shows the form at the end of the tenth interval. The curve Xa is obtained by similarly measuring off distances equal to ten times the single intervals, on normals to the planes at the original spherical surface. The difference between X and Xa shows the effect of the changing shape of the body on its further corrosion.

The actual shapes obtained are not represented exactly by either X or Xa, since the corrosion is controlled not only by the rate of solution perpendicular to certain faces but also by other factors which need not be discussed here in detail.

The more rapid dissolving of the base is confirmed by the experiments of Warburg & Tegetmeier [26] and others.

[25] GILL, A. C., Zeitschr. Kryst. (1893) **22**: 97-128.
[26] Article cited in XXVII, note [16].

The solution-forms and growth-forms produced on two quartz spheres in a hot solution of borax have been studied by Lincio,[27] using Spezia's apparatus.[28] One sphere (the upper) was placed in the "dissolving chamber," which was heated to a temperature not over 320°, while the second (lower) sphere was placed in the "growth chamber" which was kept at not less than 170°, both being immersed in a 6 per cent solution of $Na_2B_4O_7$. The action continued for 25 days. The upper sphere dissolved over most of its surface, but there were some evidences of growth on its under side. The lower sphere grew to the approximate shape of an ellipsoid of rotation with long axis vertical (prolate spheroid), but also showed some etching.

Fig. XXV.5.—Etch-figures on high-quartz at about 600°C. Friedel, 1902.

High-quartz

The etch-figures of high-quartz were first studied by Friedel.[29] He worked at 600° in order to be well above the inversion-point. Alkalies and alkaline carbonates in various fused salts did not give uniform corrosion of quartz crystals, but fused potassium acid sulfate, to which a little potassium fluoride was added as soon as the temperature reached 600°, gave clear figures. On the prism faces they consist of horizontal furrows whose faces are parallel to those of the hexagonal pyramid. On the pyramid faces (the positive and negative rhombohedrons of the low-quartz) the etch-figures are small triangles whose sides are parallel to those of the face itself, but which are pointed in the opposite direction (see Fig. XXV.5). The figures on all six faces are alike.

Mügge[30] made numerous etching experiments on high-quartz in 1907, using small plates about 1 mm thick. A repetition of Friedel's experiments confirmed his results for the most part. Instead of striations on the prism, six-sided bisymmetric pits drawn out lengthwise parallel to the base were obtained. On basal plates, first-order pyramidal pits were obtained, though they were not very distinct. Indistinct bisymmetric pits were also etched on the second-order prism. All the prism or pyramid faces of a given kind etc

[27] Lincio, G., Beitr. Kryst. Mineral. (1916) **1**: 87-101.
[28] Spezia's experiments are contained in a series of papers in Atti R. Accad. Sc. Torino, (1898) **33**: (1900) **35**; (1901) **36**; (1905) **40**; (1909) **44**.
[29] Article cited in XII, note [6].
[30] Article cited in VII, note [3].

alike. It was observed that with continued heating and volatilization of the SO_3 the temperature of the liquid could be carried up to 1200°, at which temperature the sulfate etches quartz without the aid of fluoride.

Mügge obtained better results with molten sodium metaphosphate than with potassium acid sulfate. On the pyramid faces of high-quartz the metaphosphate gave unsymmetrical triangles with their longest sides parallel to the base of the crystal. On the first-order prism the figures were parallelograms with their longer sides parallel to the base and the other sides inclined thereto at about 75°. Other faces did not give clear figures.

Nacken [31] etched 5- to 7-mm spheres of homogeneous right-quartz by embedding them in powdered sodium metaphosphate, $NaPO_3$, and heating to about 700°, the melting-point of the salt being about 610°. After 15 minutes etching the melt and sphere were cooled slowly and the salt dissolved away with water. In this manner the sphere was carried through the inversion temperature without twinning or fracturing.

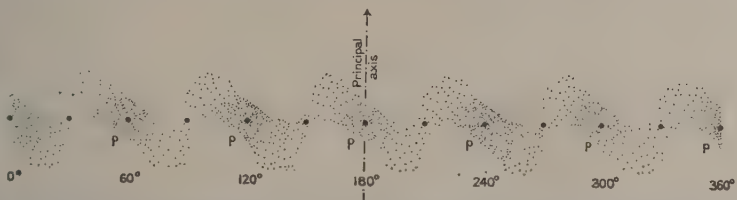


FIG. XXV.6.—Development of equatorial zone of a sphere of right-high-quartz etched with $NaPO_3$ at about 700°C. Nacken, 1916. Compare the symmetry with that of Figure XXV.2.

The results of the etching consisted of two fields of etch-figures at opposite poles of the sphere and a band of figures about the equator. The polar fields showed faintly the outline of a six-rayed star, both being alike, but one being rotated a little with respect to the other. These polar fields consisted of imperfect hexagonal pits and hillocks.

The equatorial field is represented in the sketch in Figure XXV.6. The general outline is a sixfold wave, each section of which has twofold axial symmetry. The etch-figures themselves have twofold axial symmetry but no planes of symmetry. At the middle of a field *p* they consist of elongated parallelograms whose longer dimension is at 50° to the equatorial plane. Some are completed in the bottom by four-sided surfaces, which are negative truncated pyramids. Toward the intermediate more sparsely etched regions these pits grade over into asymmetric triangular pits.

Wilson [32] has observed the rather unusual shapes of quartz illustrated in Figure XXV.7. Crystals of this kind occurred in a thin "dike" of ordinary soft glass, strongly colored with manganese, penetrating cracks in the brickwork (common brick) of a glass tank furnace which had corroded through the bottom and been drained. The dike in which quartz occurred belonged to a second stage of injection following the first solidification of the outpouring

[31] Article cited in XII, note [8].
[32] WILSON, G. V., J. Soc. Glass Techn., Trans. (1918) 2: 177-216.

glass. The habit of the crystals, only part of which are corroded, is that of high-quartz,—small short bipyramids, prism faces being either absent or small. The peculiar shapes illustrated are thought by the author to be "due rather to the growing together of small globular bodies than to subsequent corrosion." They were not found elsewhere. They may be real solution-forms, caused perhaps by a reheating of this particular dike of glass; or they may be an example of skeletal growth in quartz similar to that shown by cristobalite (see p. 506).

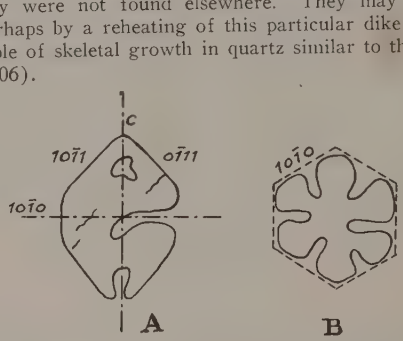


FIG. XXV.7.—Peculiar shapes of quartz observed in a dike of glass. Wilson, 1918.

THE DISSOLVING OF VITREOUS SILICA

Vitreous silica dissolves in aqueous hydrofluoric acid at a more rapid rate than quartz. Acid containing 40 per cent HF, at 20°C, dissolves about 1.6 mg per 10 sq. cm per minute from a ground surface of transparent vitreous silica, as compared with 0.46 to 0.003 mg for ground surfaces of quartz.

Experiments during the past two decades have shown clearly that the molecules in the surface of a liquid are not arranged at haphazard, as in the interior of the mass, but show definite orientation. This is particularly true of thin films, as of an oil or wax upon water. Such films, if of the proper thickness, exhibit some of the properties of a crystal one or two molecules thick. There is every reason to expect similar effects in liquid glasses, including vitreous silica. It is well known that a natural surface of a soda-lime glass acts differently from a ground and polished surface. It is not surprising, therefore, that Mügge [33] observed a much more rapid initial attack by HF on the polished surfaces of a vitreous silica plate than on its "natural" edges.

[33] p. 100 of article cited in note [24].

Part 6. Silica in the Electric and Magnetic Fields

Chapter XXVI. SILICA IN THE ELECTRIC FIELD

The dielectric constant

The capacity of an electric condenser of given dimensions differs according to the substance which is placed between the conducting plates. The ratio of its capacity, with a given substance filling the space between the plates, to the capacity in a vacuum is called the specific inductive capacity or the *dielectric constant* of the substance.

Some writers have reserved the use of the term "specific inductive capacity" for those cases where the ratio of capacities is taken with *air* as the standard instead of a vacuum. This is its original use by Faraday and should be adhered to. As so defined this constant differs from the true dielectric constant by — 0.06 per cent.

The dielectric constant of an aeolotropic substance varies with the direction of the electric field in the crystal, and with the temperature, pressure, and state of strain. If the electric field is alternating, the dielectric constant may also be expected to vary with the frequency of alternation.

The dielectric constants of silica

Low-quartz and vitreous silica are the only modifications of silica for which determinations of the dielectric constant are available.

The data on quartz are not very consistent, but all agree in showing a larger value when the direction of the lines of force is parallel to the principal axis than when it is perpendicular thereto. Low-quartz is therefore electrically, as well as optically, positive (see Table XXX.1).

The most probable values at room temperature are:

	Most probable value	Limits between which the true value certainly lies
Quartz, axis ∥ to direction of field.....	4.6	4.5 and 5.0
Quartz, axis ⊥ to direction of field.....	4.5	4.2 and 4.7
Difference (∥) — (⊥)	+ 0.1	+0.1 and +0.4
Vitreous silica	3.75	3.2 and 3.9

The experimental data on the dielectric constant of quartz

The dielectric constant of a solid substance does not seem capable of measurement with a precision greater than 0.3 per cent or an accuracy

TABLE XXVI.1.

DIELECTRIC CONSTANTS OF SILICA AS MEASURED BY DIFFERENT METHODS. JAEGER, 1917.

	Quartz. Plate ⊥ to axis				Vitreous silica			Frequency	Wave-length, meters
Specimen No.	14	15	16	(Mean of 14, 15, 16)	12	13	(Mean of 12 & 13)		
Thickness mm	1.930	2.003	2.010		2.027	1.909			
K by method I	...	4.32	4.43	4.38	3.66	3.69	3.68	250	(1 to 2) × 10^6
K by method II	4.40	4.41	4.41	4.41	3.61	3.71	3.66	10^5	3000
K by method III	4.40	4.37	4.40	4.39	3.58	3.59	3.59	10^6	300
K by method IV	...	4.34	4.43	4.39	3.57	3.56	3.57	10^7	30 to 40
K by method V	4.695	...	...	4.70	3.80	3.80	3.80	3×10^7	10
K by method VI	...	4.65	...	4.65	3.72	...	3.72	10^5	3000
Mean of two groups of methods *				4.58			3.72		

* The mean of methods V and VI is given double weight as compared with the mean of methods I to IV. The values differ a little from the values published by the author, as there seem to have been some errors of transcription in his summarized table. (Confirmed by correspondence.)

greater than 1 per cent, and both precision and accuracy have usually been much poorer than this.

The principal determinations upon which an estimate of the most probable values for quartz must be based are classifiable into 3 groups, depending upon:

(*A*) Measurement of the capacity of a plate condenser containing quartz; J. Curie (1888), Curtis (1912), Rubens (1915), Richardson (1915), R. Jaeger (1917).

(*B*) Measurement of the capacity of a condenser containing a liquid having the same dielectric constant as quartz; Starke (1897), Ferry (1897), W. Schmidt (1902).

(*C*) Measurement of the forces acting on a fragment of quartz in an electric field; Romich & Nowak (1874), Fellinger (1902), Thornton (1910).

The data on quartz are not very satisfactory. Some of the investigations have yielded results which were admittedly not of high accuracy. Others seem to be both precise and accurate, and yet different observers using different specimens get values which do not agree well. There is not evidence enough to show whether these differences are due to hidden errors in apparatus and methods, or whether they represent real variations among the specimens. Further study of this point is desirable.

(A) Measurements with plate condensers

The most thorough piece of work by method (*A*) on the dielectric constants of silica in recent years is that of R. Jaeger.[1] He tested a number of substances in plate condensers, including quartz and vitreous silica, using 6 different methods for the measurement of the capacity. The first four methods served to give comparative values at several different frequencies, with other variables left unchanged; while the last two furnished absolute measurements of the constant.

The methods used were:

I. Maxwell's method, in which the condenser is alternately charged and short-circuited while acting as one arm of a Wheatstone bridge.

II. Thomson's oscillatory circuit with Poulsen arc excitation. The Thomson circuit consists of a self-induction in series with a capacity, the capacity in the present case consisting of the unknown and a known variable condenser in parallel. Resonance was detected by means of an aperiodically damped detector circuit with direct-current galvanometer and silicon contact detector.

III. Thomson oscillatory circuit with quenched spark excitation. The oscillatory circuit and detector circuit are the same as described above.

IV. Lecher's method. The Lecher circuit consists of two long parallel wires bridged at one end by a variable condenser; the wave-length of the stationary waves in the system is measured with the help of a detector such

[1] JAEGER, R., *Die Dielektrizitätskonstante fester Körper bei verschiedenen Wellenlängen*, Dissertation, Berlin, 1917. 75 pp.

as a gas tube. In the present instance the circuit consisted of the two wires bridged at one end by a variable condenser, in the middle by a bridge, and at the farther end by the unknown and a known variable condenser in parallel. Resonance was produced by adjustment of the condensers. The excitation was electrostatic, by means of zinc plates at the terminals of an induction coil. The detector was either a neon lamp or a thermel with direct-current galvanometer.

V. Lecher circuit with adjustable plate condenser. In this arrangement a condenser having an adjustable plate takes the place of the two condensers in parallel described under IV. Resonance is first produced with a plate of the substance in the condenser, and again by resetting after the specimen has been removed.

VI. Thomson circuit with adjustable plate condenser as in V, and Poulsen arc excitation.

Kirchhoff's formula for circular plate condensers was first experimentally confirmed by a series of measurements, and values of the dielectric constant were then obtained by the methods outlined above. The results on quartz and vitreous silica are shown in Table XXVI.1.

J. Curie [2] was the first to obtain an exact measure of the dielectric constant of quartz in its two directions. He used a plate of quartz coated with a metallic coating, and compared the capacity of the condenser so formed with the capacity of an air condenser of like dimensions, through neutralizing the charges by means of his newly-devised piezo-electric quartz plate. The necessity of an absolute measure of the potentials is thereby avoided.

Preliminary measurements gave values which varied as much as 5 per cent, leaving undetermined even the question whether the parallel or the perpendicular constant is the larger. Further experiments of greater precision, made on 4 larger plates, gave the following results:

Plate	Thickness mm	Area sq. cm	K	Mean K
(a) ∥ to threefold axis, ∥ to twofold axis	0.674	19.197	4.47	4.49
(b) ∥ " " " ⊥ " " "	2.164	12.61	4.515	
(c) ⊥ " " "	0.697	12.593	4.55	4.55
(d) ⊥ " " "	1.065	6.557	4.56	

No reason was found for the discrepancy between the two plates parallel to the axis.

Curie tested also the effect of a relatively small change of frequency, with the following results:

	Charging time 0.02 sec.	Charging time 1 sec.
Plate (b) ∥ to axis.....	4.515	4.55
" (c) ⊥ to axis.....	4.54	4.60

[2] CURIE, JACQUES, *Recherches sur le pouvoir inducteur spécifique et la conductibilité des corps cristallisés.* Thèse, Paris, 1888. 64 pp. Also Ann. Chim. et Phys. 1889 (6) 17: 385-434.

The difference is probably due to hidden errors in the method, as no such effect of frequency has been confirmed by later observers.

Rubens [3] measured the dielectric constant of quartz by Lecher's method with adjustable plate condenser (see V, above). The following results were obtained on plates of quartz perpendicular to the axis, and at a frequency of (20 to 30) $\times 10^6$, corresponding to a wave-length of 10 to 15 meters.

Thickness mm	K
1.93	4.62
3.99	4.69
Mean	4.65

Curtis [4] used thin plates of various minerals, including quartz, in a plate condenser with a guard ring, and measured the capacity by two methods: (1) by direct current, alternately charging the condenser and storing its charge, by means of motor-operated connections, in an air condenser of large capacity, whence it was withdrawn through a measuring galvanometer; (2) by alternating current, with a Thomson circuit (see method VI, above) and wave meter. The constant found for quartz is 4.9; the orientation was unfortunately not recorded.

In the course of his work on the residual charge and conductivity of quartz, Richardson [5] determined the dielectric constant in the axial direction to be 4.6 at 26.5°C. The measurements were made with a plate condenser consisting of a disk of quartz 1.8 mm thick cut perpendicular to the axis and silvered over an area of 29.7 sq. cm on both faces, the edge being also silvered for use as a guard ring. The charge was measured with the aid of a calibrated condenser of large capacity and an electrometer. The apparatus was contained within an inclosure held at constant temperature and dried with calcium chloride.

(*B*) *Method of liquid replacement*

The determinations grouped under (*B*), p. 517, depend upon a principle suggested by Starke.[6] A liquid mixture is prepared of such composition that the insertion of a plate of quartz does not change the capacity of the condenser cell containing the liquid. The dielectric constant of the liquid, which is then identical with that of the specimen, may be measured independently.

Starke's own measurements on quartz, about which no details were published, apparently yielded the same value, 4.73, for directions parallel and perpendicular to the axis.

[3] Rubens, H., *Über Reflexionsvermögen und Dielektrizitätskonstante isolierender fester Körper und einiger Flüssigkeiten,* Sitzungsber. Preuss. Akad. Wiss. Berlin 1915: 4-20, 1 pl.

[4] Curtis, H. L., *The dielectric constant, resistivity and electrostatic absorption of different crystals,* Physical Rev. 1912, **34**: 154-155.

[5] Richardson, S. W., *Some experiments on the properties of dielectrics,* Proc. Roy. Soc. London (1915) A, **92**: 41-57.

[6] Starke, H., Ann. Phys. u. Chem. (Wiedemann) 1897, **60**: 629-641.

Ferry[7] measured the two constants of quartz both at a high and at a low frequency, using Starke's principle, but with two different methods for the capacity. The high-frequency capacity was determined by equating the capacity of the cell to that of a variable air condenser through the adjustment to resonance of two Thomson circuits which were coupled to a third in which a high frequency current was maintained.

For low frequency Ferry used the method of Nernst, depending upon the balancing of four condensers in a Wheatstone bridge with a small induction coil and telephone.

The results obtained are as follows:

Frequency	Field ∥ to axis	Field ⊥ to axis
33×10^6	4.34 ± 0.01	4.27 ± 0.01
20	4.46	4.38

W. Schmidt[8] also measured the constants of quartz by Starke's method of liquid replacement, but gained additional precision by finding the intersection of two empirical capacity curves instead of measuring a single capacity. The measurement is based upon the known dielectric constants of a series of liquid mixtures. The first curve is in effect a curve of the measured capacities of a condenser with fixed electrodes containing the series of liquids, plotted against the dielectric constants of those liquids. The second curve is similar except that the liquid between the electrodes is partly replaced by the specimen plate. The intersection of the two curves represents the condition where specimen and liquid have the same dielectric constant.

The relative change of capacity was read by means of a Lecher circuit, in two ways: (1) by the use of Drude's device of "telescoping" the wires to vary the self-inductance, and (2) by the use of an independent secondary Lecher circuit with movable bridge. It was thus possible to observe the effect of a change of frequency although the change is relatively not large. The results on quartz are:

	Field ∥ to axis	Field ⊥ to axis
Method (1)	4.60	4.36
Method (2)	4.60	4.32

(C) Measurement of forces on a fragment

A fragment of an insulator, when placed in an electric field, tends to orient itself with its long dimension parallel to the field. The orienting force depends upon the dielectric constant.

A disturbing influence in any method depending on this principle is

[7] FERRY, E. S., *The specific inductive capacity of dielectrics in slowly and rapidly changing electric fields*, Phil. Mag. 1897, (5) **44**: 404-414.

[8] SCHMIDT, W., *Bestimmung der Dielektricitätsconstanten von Krystallen mit elektrischen Wellen*, Ann. Physik (4) (1902) **9**: 919-937.

the presence of pyroelectric charges which persist for a long time and may be renewed by small irregularities of temperature.

Fellinger[9] measured the dielectric constants of quartz by the method of Graetz & Fomm. He used bars of quartz about 20×2.5 mm, cut parallel and perpendicular to the axis, and measured their deflection as controlled by a suspension of known torsional moment. The field was produced by an alternating voltage of 70 to 80 volts on a Kohlrausch condenser between whose plates the bar was suspended. The results are:

Field $\parallel$ to axis.....	$K_1 = 5.056$
Field $\perp$ to axis.....	$K_2 = 4.695$

Thornton,[10] instead of measuring the torsional force directly, obtained greater precision by measuring the period of oscillation of long ellipsoids suspended by vitreous silica fibers. The period of a quartz ellipsoid depends upon the combined effects of the torsion of the fiber and the electric restoring couple expressible in terms of the two dielectric constants of quartz. Two ellipsoids of rotation, about 20×2.3 mm, accurately shaped, and cut with long axes parallel and perpendicular to the axis, respectively, were observed in an evacuated dry vessel, when suspended between metal electrodes which supplied an alternating field having a frequency of about 80 cycles per second. The period of the oscillations was one second or more. The method is capable of high precision and should be quite accurate if the disturbing effects of pyroelectricity and possible errors of orientation can be eliminated. The results obtained by Thornton are:

Quartz, Field $\parallel$ to axis.....	4.600
Quartz, Field $\perp$ to axis.....	4.5485
Vitreous silica	3.78

The earliest measurement of the dielectric constant of quartz is that by Romich & Nowak,[11] who used Boltzmann's method of comparing the force of translation exerted upon a small sphere in an electric field with the force exerted upon a metal-coated sphere in the same position. Apparently no attempt was made to distinguish between the two constants of quartz. The result, 4.6 at 64 cycles per second, was not considered very exact because of the large dielectric anomaly, the quartz sphere being attracted in a static field nearly as strongly as a metallic sphere.

Experimental data on the dielectric constant of vitreous silica

Schulze[12] measured the dielectric constant of the specimen of vitreous silica on which he had determined the elastic constants and the refractivity (see

[9] Fellinger, Robert, *Bestimmung der Dielektricitätsconstanten von Krystallen in homogenen elektrischen Felde,* Ann. Physik (4) (1902) **7**: 333-357.

[10] Thornton, W. M., *The measurement of dielectric constants by the oscillations of ellipsoids and cylinders in a field of force,* Proc. Roy. Soc. London (1909) A, **82**: 422-447.

[11] Romich & Nowak, *Experimentaluntersuchung dielektrischer Körper in Bezug auf ihre dielektrische Nachwirkung,* Sitzungsber. Kais. Akad. Wiss. Wien, Mat. Nat. Kl. (1874) **70** II: 380-407.

[12] Article cited in XXIII, note [10].

p. 440). He used the method of Drude, as modified by W. Schmidt (see p. 520) and obtained the value 3.20.

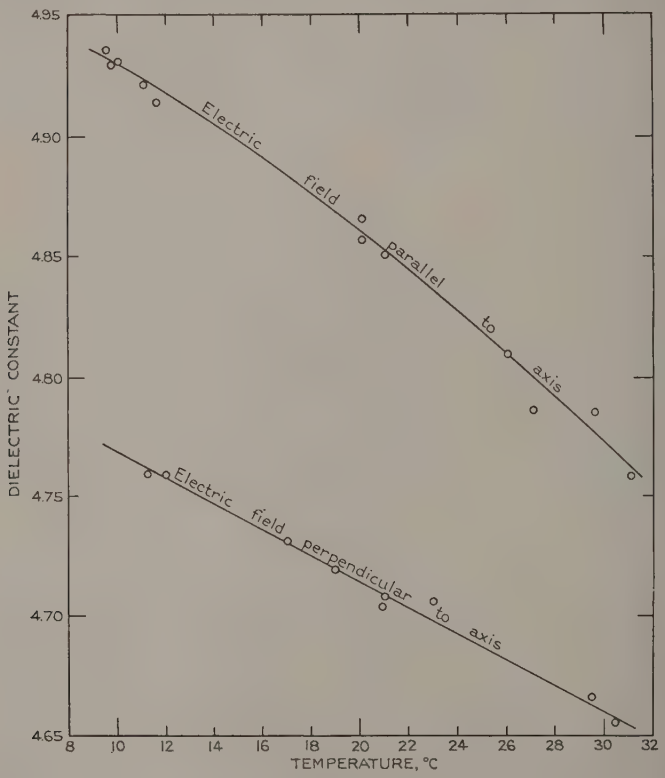


FIG. XXVI.1.—Apparent change of dielectric constants of quartz with temperature. Hasenoehrl, 1897.

The constant has also been measured by Jaeger and by Thornton (see notes [1] and [10]). The results are assembled here for comparison:

Schulze	3.20
Thornton	3.78
Jaeger	3.72

I have adopted as the most probable value the mean of Thornton's and Jaeger's determinations.

Rubens [13] showed that measurements of the dielectric constant of silicate

[13] RUBENS, H., Sitzungsber. K. Pr. Akad. Berlin 1916: 1280-1293.

glasses at low frequencies may be subject to considerable error from the effect of conducting surface films, especially if the glass be one of those varieties which are not very resistant to weathering. This error is practically eliminated in the case of vitreous silica because of its small absorption of water and its freedom from oxides which might produce conducting solutions.

Temperature coefficient of the dielectric constant

A measurement of the temperature coefficient of the dielectric constants of quartz has been made at room temperatures by Hasenoehrl.[14] He used the Gordon-Lecher method (see page 518) for determining the capacity. The plates were coated with metal foil and tested in a thermostat in the range 10 to 31°C.

A small plate of thickness 4.13 mm, coatings 11.5 mm diameter, cut perpendicular to the axis, gave results of rather low precision, with an average value for the temperature coefficient of — 0.135 per cent. Better results were obtained with two exactly similar plates 5.07 mm thick, with coatings 14.55 mm in diameter, one perpendicular and the other parallel to the axis. The data are plotted in Figure XXVI.1 and are represented empirically by the formulas:

$$K_{\parallel} = 4.926\ [1 - 0.00110(t - 10) - 0.000\,024(t - 10)^2]$$
$$K_{\perp} = 4.766\ [1 - 0.00099(t - 10)]$$

The accuracy of the coefficient is of course greater than that of the absolute values of K, which can not be obtained very accurately by this method. To a somewhat less degree it is also true that the ratio of $K_{\parallel}$ to $K_{\perp}$ is more accurate than the absolute values.

The most extensive experiments on the effect of temperature on the dielectric constant are those of Gagnebin.[15] He used a resonance method similar in principle to that of Ferry,[16] but employing triode tubes for the control of the frequency. The resonating circuit served both as standard of frequency and as detector.

Both the conduction current and the anomalous charge and discharge current (see XXVII) become fairly large at the higher temperatures reached in the investigation. These currents could not be directly determined, and were therefore estimated from their effect on the amplitude of the oscillating current, this effect being separately determined by studying the corrections necessary when a non-inductive resistance was introduced in parallel with the adjustable condenser. The effect of the conduction current is fairly definite, but it was necessary to make an unproved assumption concerning the anomalous currents, namely, that the same relation holds between the diminution of amplitude and the correction, whether the energy absorbed is due only to conduction or to conduction combined with anomalous currents. This introduces into the results an uncertainty which increases with the temperature.

Three series each were made on plates perpendicular and parallel to the

[14] Hasenoehrl, F., *Über den Temperaturcoefficienten der Dielektricitätsconstante in festen Isolatoren,* Sitzungsber. Kais. Akad. Wiss. Wien, Mat. Nat. Kl. (1897) **106,** IIa: 69-82.

[15] Gagnebin, S., *Recherches expérimentales sur la variation thermique des constants dielectriques du quartz cristallisé,* Arch. sci. phys. nat. (1924) (5) **6**: 161-210.

[16] Ferry, E. S., article cited in note [7].

axis, at temperatures up to 800°, and at a frequency of 21,000 to 21,500 per second. As the measurements are comparative and not absolute, Ferry's values at room temperature were taken as the basis. The results of the third series, for each direction, were considered to be the best of the three, and are shown in Figure XXVI.2.

The dielectric constant in the direction perpendicular to the axis changes very little up to about 550°. It then begins to rise rapidly and approaches a constant value of about 12.

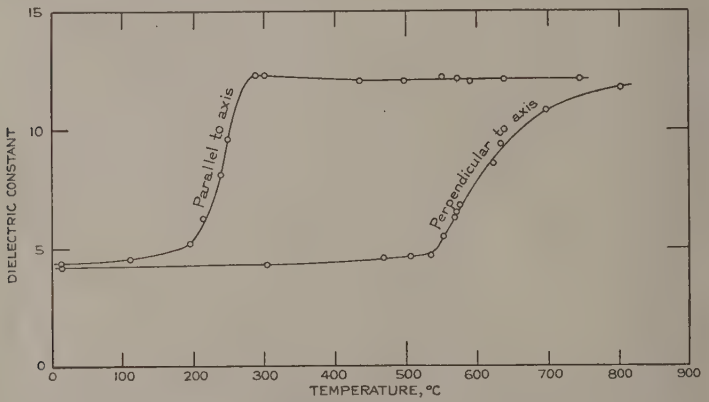


FIG. XXVI.2.—Change of dielectric constants of quartz with temperature. Gagnebin, 1924.

The constant parallel to the axis shows a similar kind of change, but at a different temperature. It increases but little to 150 or 200°, and then rises rapidly to reach another constant value at 300° which is practically the same as the high-temperature value of the $\perp$ constant.

The abnormally large conductivity of natural quartz parallel to the axis throws some doubt on the reality of this second change. The doubt would be greater if the change were a gradual one over the range from 200 to 800°, but the change is not gradual; it has all the appearance of a real inversion. On the other hand, the apparent inversion is at a temperature which would never have been expected for quartz, and for which there is no parallel in any other property.

DIELECTRIC ANOMALIES

Thus far, the dielectric constant has been considered as representing the instantaneous reaction of the substance to the electric field. But just as the simple doctrine of elasticity had to be taken (see p. 451) as representing only an ideal limiting state approached but not quite attained by actual substances, so the simple definition of the dielectric constant has to be taken as an ideal limiting case, the *time* of charge and discharge entering into the phenomena in actual substances.

The dielectric properties of a gas are comparatively simple. The polarization is practically instantaneous, and is a definite function of the field. This is not true of solid and liquid dielectrics. The polarization is not instantaneously produced, and is a function not only of the field, but also of the time.

The effects are best described [1] in terms of the current which is flowing at any instant under conditions of constant or only slowly changing potential difference. The effects of an alternating p. d. follow directly from these according to well-known principles. The current under the conditions stated is divisible into three parts:

A. The normal charging current, which can be made practically instantaneous;

B. The anomalous charging or discharging current, which is a function of the time;

C. The conduction current, which is independent of time except as the potential varies with the time.

A. THE NORMAL CHARGING CURRENT

This needs no special discussion. The nearly instantaneous charge delivered by it is expressed in terms of the true dielectric constant, on which data have already been given in XXVI.

B. THE ANOMALOUS CURRENTS

The phenomena of the anomalous current are further divisible into (a) irreversible phenomena and (b) reversible phenomena.

(a) The irreversible anomalous charging current in a condenser represents the transport of electricity which is not recoverable when the condenser is discharged. It represents electric energy which is being converted into heat and which therefore does not remain available for complete reconversion into electric energy.

[1] See SCHWEIDLER, E. v., Graetz's *Handbuch d. Elektrizität* (1918, Leipzig) Vol. 1, pp. 232-261.

(b) The reversible anomalous charging current, on the other hand, represents the transport of electric energy which is recoverable when the condenser is discharged.

The irreversible charging phenomena cause a continuous loss of electric energy when a condenser is charged and discharged repeatedly, as by an alternating potential; while the reversible phenomena cause the apparent capacity to vary with the frequency and to differ from the true capacity. The anomalous effects in general, and the reversible anomalous effects in particular, are therefore often included under the general term "dielectric hysteresis," by analogy with magnetic hysteresis.

Logical usage, however, would retain the term "hysteresis" only for cases where time effects do not enter. The distinction is often recognized by the use of the terms "true hysteresis" and "viscous hysteresis," the latter containing the time as a factor.

It is not yet proved that there is any such thing as a true dielectric hysteresis corresponding to magnetic hysteresis and independent of time. There is little question, on the other hand, of the existence of a time effect in the dielectric displacement; it is best referred to as *dielectric after-effect.*

Anomalous currents in silica

Quartz and vitreous silica show both irreversible and reversible dielectric anomalies, but the data are not sufficiently abundant of any one kind —though quite varied in character—to permit of their logical arrangement in support of general conclusions. The principal effects are of the reversible type, and are more considerable in quartz than in vitreous silica. Furthermore, the anomalies in quartz are much greater when the field is parallel to the axis than when it is perpendicular thereto.

C. The conduction current

When two terminals, supplied by a source of electric energy, and differing in potential, are placed in contact with a solid or liquid substance, an electric current flows between them through the substance. When the current is made to flow uniformly through a cylindrical portion of the substance between the two electrodes, and a steady state of flow has been attained, the current is found to be exactly proportional to the potential difference (voltage) for all ordinary magnitudes of either current or voltage. This is the experimental principle known as *Ohm's Law.* The constant ratio of current to voltage is called the *conductance,* and the mathematical reciprocal of this quantity is the *resistance.*

If the voltage is applied between opposite faces of a cube $1\times1\times1$ cm, this constant ratio is called the *conductivity* of the substance, and its reciprocal is called the *resistivity.* The conductivity can be calculated from the conductance of a piece of other dimensions by virtue of the fact

that the conductance is proportional to the cross-sectional area and inversely proportional to the length.

The conductivity of all substances varies with the temperature and the pressure. Furthermore, the conductivity of an aeolotropic substance varies with the direction of the current in the substance. The symmetry of quartz, the only crystalline modification which has been studied, requires that there be two principal conductivities, one axial or parallel to the axis, and the other equatorial or perpendicular to the axis.

Conductivity of silica

Silica in all its modifications is an almost complete non-conductor at room temperature, and a very poor conductor even at fairly high temperatures. Measurable and reasonably reproducible constants having the nature of true conductivities are, nevertheless, obtainable.

The difficulty in defining the electric conductivity of any modification of silica—quartz, for example—lies in the impossibility of establishing experimentally the conditions under which Ohm's Law is defined. Electrodes can be placed in contact with a cubical specimen and a constant potential difference can be set up between them, but the steady state of flow is attained only after the lapse of some hours or days, and when it is established at one voltage the current at another voltage cannot always be predicted from the first by simple proportion, as Ohm's Law requires. The "conductivity" (or "resistivity") of quartz is, then, not a constant characteristic of the substance to the same degree that the conductivity of a metal or an electrolytic solution are characteristic. The conditions of measurement need to be carefully stated in order to give the figure a meaning.

We probably come nearest the true conductivity as expressed in the conduction current (portion C, page 525) by taking the value of current and voltage after the lapse of a time interval sufficient to bring the current nearly or quite to constancy.

Quartz

Even when measurements have been made under carefully defined conditions, there still remains considerable doubt as to the true values of the conductivities of quartz. The difficulty lies mostly in the peculiar character of the axial conductivity of *natural* quartz, the only kind which has been studied. At temperatures of several hundred degrees this conductivity is largely electrolytic, and apparently due to very small quantities of foreign substances, present in the crystal and undergoing complex changes during the course of the measurements.

The measured axial conductivity is, therefore, not the axial conductivity of the pure substance SiO_2 in the crystalline form known as quartz, but

is the conductivity of an impure crystal. The true axial conductivity of the pure crystal is quite unknown.

The equatorial conductivity of natural quartz is very much smaller than the measured axial, and of a very different quality. It is not so tied up with the presence of impurities as the axial, and may be "metallic" in character, that is, not associated with any transport of atoms or ions.

The conductivity of vitreous silica is similar in character to the equatorial conductivity of quartz. Its order of magnitude and its change with temperature are reasonably well known.

Table XXVII.1 contains an estimate of the most probable values for the electric resistivities of quartz and vitreous silica at various temperatures, as judged from the permanent conduction current or from other data supposedly independent of the anomalous charging current. Resistivity is given in the Table rather than conductivity, since the conducting properties of insulators are more commonly expressed in this form.

The resistivity decreases (conductivity increases) rapidly with increasing temperature, and the conduction current therefore becomes a larger and larger part of the total current observed at any instant, as the temperature becomes higher.

TABLE XXVII.1.

APPROXIMATE RESISTIVITIES OF QUARTZ AND VITREOUS SILICA AT VARIOUS TEMPERATURES.

Ohms per sq. cm per cm.

t °C	Quartz ∥ to axis *	Quartz ⊥ to axis	Vitreous silica
20	0.1×10^{15}	20×10^{15}	10×10^{15}
100	0.8×10^{12}		1×10^{12}
200	70×10^{9}		10×10^{15}
300	60×10^{6}		0.2×10^{12}
400			5×10^{9}
500			0.3×10^{9}
600			60×10^{6}
700			10×10^{6}
800			4×10^{6}
900			2×10^{6}
1000	50×10^{3}	100×10^{3}	1×10^{6}
1100			0.7×10^{6}
1200			0.5×10^{6}
1300	5×10^{3}	10×10^{3}	0.4×10^{6}

* This is natural quartz, whose axial conductance is due mainly to impurities; the true axial resistivity of pure quartz is not known.

THE EXPERIMENTAL DATA ON STORAGE AND FLOW OF ELECTRICITY IN QUARTZ

The observed currents in quartz increase very rapidly with temperature; hence the most natural subdivision of the data is a subdivision according to the range of temperature covered by the experiments. Not all the

data, however, are equally useful in obtaining a general view of the phenomena. From the discussion which has preceded, it will be evident that measurements in which the time of flow of the current has not been accurately measured are of much less value than those in which the time has been taken into account.

Data on quartz at room temperature only are supplied by the experiments of Thornton (1910), Shaposhnikov (1910), Curtis (1912), Richardson (1915), and Saegusa (1921).

Quartz at temperatures of 100 to 500° has been studied by J. Curie (1886-1888), Tegetmeier & Warburg (1887-1890), Exner (1901), and Ambronn (1915).

Measurements above 500° have been made by Doelter (1908-1910).

Measurements at room temperature

Thornton.—Thornton's [2] experiments seem very carefully made and reliable. His method depends upon the determination of the restoring couple on an ellipsoid oscillating in a stationary field (see also XXVI). Observations were made on ellipsoidal rods of vitreous silica and of quartz parallel and perpendicular to the axis, of dimensions about 20×2 mm, suspended by vitreous silica fibers in a carefully dried inclosure between metal plates, with fields of 0.09 to 0.75 e. s. u. The precision of the method is high, being about 0.1 per cent.

Three stages are observed with most dielectrics: (1) a fairly rapid change lasting several seconds or a minute; (2) a stage which may continue several hours, and in which the increase in polarization is nearly proportional to the time; (3) a stage which may last several days and in which the increase falls off gradually as the polarization approaches a fixed value. The complete series in quartz and vitreous silica are illustrated by Figure XXVII.1, in which I have included all the data, Thornton having represented only the early stages. The scale is log: log. The diagram brings out the contrast between the earlier and later stages.

The polarization parallel to the axis becomes quite large, as Romich & Nowak had already observed qualitatively.[3] This is evident from the Figure and also from the data in Table XXVII.2, obtained in a field of about 0.265 e.s.u. except where otherwise stated.

It is interesting to note that the final value which the polarization approaches seems to be independent of the field, between the limits 0.09 and 0.75 e. s. u.

The dielectric anomaly expressed in the delayed charging of the quartz ellipsoid may be expressed in terms of electric conductivity. As Thornton shows, this changing polarization of the ellipsoid in a stationary field is, in effect, a current whose density is the rate of change of the total polarization in unit volume. The conductivity so obtained is evidently not identical with that corresponding to the definition in terms of Ohm's Law, because as the dielectric polarization approaches a steady value the apparent conductivity approaches zero. But until it can be shown that the flow of current in silica does obey Ohm's Law we must take advantage of whatever data are available

[2] THORNTON, W. M., *The polarization of dielectrics in a steady field of force,* Phil. Mag. (1910) (6) **19**: 390-407.

[3] See XXVI, note [11].

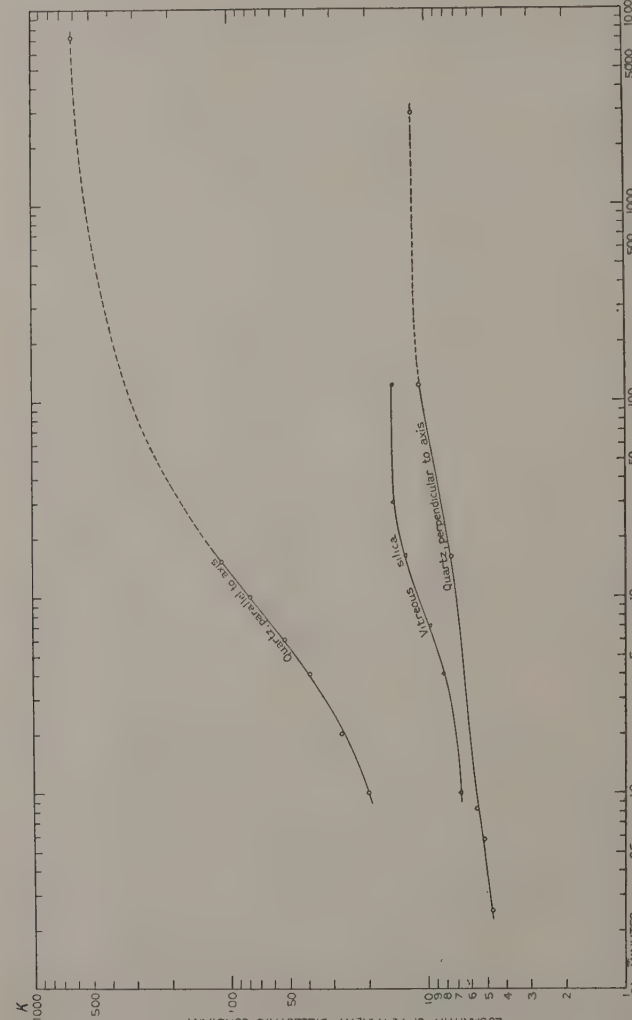


FIG. XXVII.1.—Change of dielectric polarization of quartz and vitreous silica with time. Data of Thornton, 1910.

TABLE XXVII.2.

PART OF THORNTON'S DATA ON ANOMALOUS CURRENTS IN SILICA.

	Time	Apparent K
Quartz ellipsoid ‖ to axis	1 min.	20
	10 min.	78
	144 hrs.*	508 †
		610 ‡
Quartz ellipsoid ⊥ to axis	1 min.	5.7
	48 hrs.	11.66
Vitreous silica ellipsoid	1 min.	6.8
	2 hrs.	14.7

* 120 hours at 0.137 followed by 24 hours at 0.266 e.s.u.
† Measured in field of 0.266 e.s.u.
‡ " " " " 0.137 e.s.u.

on electric displacement and potential difference, and deduce values of conductivity as if Ohm's Law held. Conductivities obtained by the leakage method

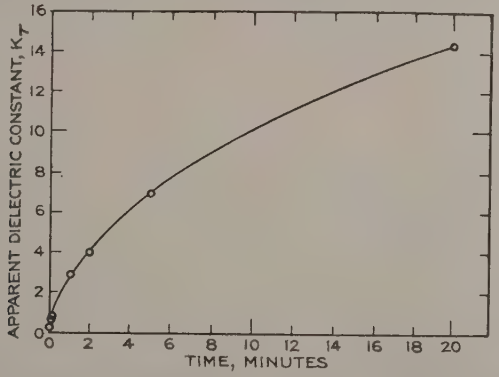


FIG. XXVII.2.—Relation of reversibly stored charge to time of charging in quartz, with axis ‖ to field. Temperature 26.5°C. Richardson, 1915.

are open to similar objections, and, at least, the results are worth comparing.

From the rate of change of dielectric polarization during the linear stage of change (see p. 529) Thornton obtained the following values of electric resistivity at 17°C:

Quartz, direction ‖ to axis	0.153×10^{15}	ohms
" " ⊥ " "	20×10^{15}	"
Vitreous silica	1.6×10^{15}	"

Ratio quartz ⊥ /quartz ‖, 131

Richardson.—Richardson's [4] first experiments were concerned only with the reversible anomaly, and were confined to quartz oriented with axis parallel to the field (plate cut perpendicular to the axis). He measured the residual charge

[4] RICHARDSON, S. W., article cited in XXVI, note [5].

in a plate condenser containing a plate of quartz, as influenced by the time of charging in a stationary field, through the medium of measuring the discharge rate at various intervals after the beginning of the discharge. The discharge rate was measured by carrying off the charge during a given interval to a condenser of large capacity connected to an electrometer.

The quartz plate stores a charge which can be considered as consisting of two portions: (1) a portion which is discharged instantaneously when the plates are connected after a short interval τ after the charging has been inter-

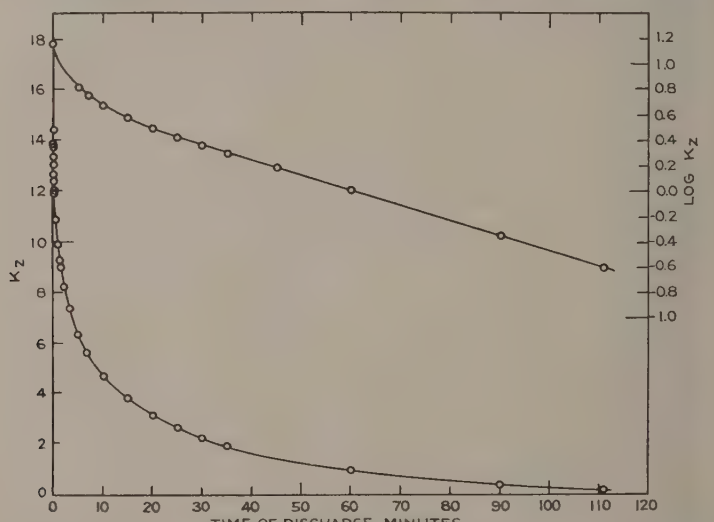


FIG. XXVII.3.—Typical curve of rate of discharge of reversibly stored charge in quartz, with axis || to field. Temperature 26.5°C. Time of charging 20 minutes. Richardson, 1915.

rupted; (2) a portion which is given out only slowly while the plates remain connected. The total quantity, Q, can therefore be represented by

$$Q = (K + K_\tau)CV$$

where C is the geometrical capacity (capacity in a vacuum without the quartz), V is the potential difference, K is the dielectric constant as determined by instantaneous discharge, and K_τ is the corresponding constant belonging to the reversibly stored charge.

K_τ increases with the time of charging in the manner shown in Figure XXVII.2.

The rate of discharge depends upon the quantity stored (expressed by K_τ) and therefore upon the time of charging. A typical curve of discharge rate is shown in Figure XXVII.3, in which the quantity remaining stored at any time is expressed by a constant K_z, analogous to K_τ. The upper curve is

logarithmic; the lower, direct. Similar curves of discharge were obtained after charging-periods of 3 seconds, 2 minutes, and 5 minutes.

K_z is related to K_τ by an expression of the form

$$K_z = nK_\tau e^{x - \alpha z}$$

in which n is a constant, e is the logarithmic base, x is an exponential function of the time, and α is a constant for a given time of charging. The complete analytical expression of the discharge rate has not been worked out. n has the value 0.36 for quartz with axis parallel to the field.

A second set of experiments[5] was concerned with the anomalous charging current. When the plate has been charging for a given time at a certain potential and this is suddenly decreased, a value of the potential can be found such that no further current flows to the plate. If it is decreased below this value a current will flow in the opposite direction. In quartz (axial direction) this "electromotive force of polarization" rises in a few seconds to a nearly constant value.

Richardson calculated the resistivity of quartz at 26.5° in the axial direction (plate $\perp$ to axis) from the foregoing observations. The charging current I at any moment is considered to be represented by the equation

$$I = \frac{dQ}{dz} + \frac{E-P}{R}$$

where dQ/dz is the rate at which the charge is accumulating in the plate; E is the applied e. m. f.; P is an assumed "e. m. f. of polarization" or opposing e. m. f. in the quartz; R is the true electric resistance of the quartz.

The method gives consistent values of R for times of charging varying from 10 seconds to 20 minutes. The results are shown in Table XXVII.3. All of the electric units in the table are c. g. s. electromagnetic,[6] being referred to the constant voltage $V = 1$.

From the mean value the resistivity is calculated to be 20×10^{21} e. m. u. or 20×10^{12} ohms.

Similar experiments on a plate cut parallel to the axis[7] gave a resistivity of 4.3×10^{24} units or 4.3×10^{15} ohms.

Saegusa.—A detailed examination of the dielectric anomalies of quartz under stationary potentials has been made recently by Saegusa.[8] Plates of quartz perpendicular to the axis, and also parallel to the axis and to $(10\bar{1}0)$, of thicknesses 0.33 and 0.48 mm, respectively, were used in a plate condenser in a dry inclosure at temperatures of 7 to 27°C. Most of the measurements were at 17°. The delayed charging current and the residual charge were studied through the medium of the change in potential with time of the insulated condenser, by means of a Dolezalek quadrant electrometer. The rever-

[5] RICHARDSON, S. W., *The flow of electricity through dielectrics,* Proc. Roy. Soc. London (1915) A, **92**: 101-107.

[6] Correspondence with the author.

[7] RICHARDSON, S. W., Proc. Roy. Soc. Lond. (1925) **A 107**: 101-112.

[8] SAEGUSA, H., *On dielectric hysteresis and allied phenomena,* Sci. Rep. Tohoku Imp. Univ., First Series (1921) **10**: 101-116, 14 pls.

TABLE XXVII.3.

CHARGING PHENOMENA WITH QUARTZ PLATE CUT PERPENDICULAR TO AXIS. RICHARDSON, 1915.

$t = 26.5°$ C. Plate is 1.8 mm thick, with silvered area of 29.7 sq. cm.

Time of charging Minutes	Current $10^{21} I$	Rate $\frac{dQ}{dt} \times 10^{21}$	Polarization P	Apparent resistance $\times 10^{-18}$	True resistance $10^{-18} K$
20	1.64	0.09	0.82	610	116
5	1.68	0.20	0.81	595	128
2	1.92	0.28	0.80	520	122
1	2.08	0.39	0.80	481	118
⅙	3.80	0.88	0.65	263	120
					Mean 121

sible and irreversible cyclic effects, the so-called "hysteresis," were studied by means of a cycle of steps of charging or discharging the condenser containing the specimen, with the aid of a supplementary air condenser.

The irreversible cyclic effect is termed by Saegusa "stationary hysteresis," and the reversible, "plastic hysteresis." When the steps of the cycle are made at intervals of less than one hour in charging, or fifteen minutes in discharging, the curve loop is due mainly to the reversible currents. If there were no irreversible effects this loop would shrink to zero area when the intervals between steps became one hour or fifteen minutes, respectively. The fact that a narrow loop still persists even with intervals longer than those just stated is taken as evidence of the existence of an irreversible effect.

When correction is made for leakage, it is found that the insulated condenser attains a permanent potential difference in about an hour, after being charged for 2 minutes. Similarly, after being charged for 4 minutes and discharged for 5 seconds, its potential difference rises to a permanent value in about 15 minutes. The relation of these final values to the original potential difference, in clear quartz, is at first linear, but the final value becomes less than proportional at higher potentials. The upper limits of the linear relation, in volts per mm thickness, are:

	Clear quartz from Yamanashi		Black quartz from Yamanashi	
	Field ∥ to axis	Field ⊥ to axis	Field ∥ to axis	Field ⊥ to axis
Delayed charging	333	542	83	481
Residual charge	315	532	51	486

Saegusa's "plastic hysteresis" is found by him throughout the range of potentials, but "stationary hysteresis" appears only at potentials above the limit of proportionality given above.

The anomalies in quartz when the field is parallel to the axis are about ten times as large as when the field is perpendicular thereto.

The anomalies, both reversible and irreversible, are much larger in black quartz than in clear quartz. This is particularly true for fields parallel to the axis.[9]

The general criticism may be made of Saegusa's results, that in every case he corrects the readings by deduction of a "leakage" which is assumed to be identical with the permanent value attained after an hour or more by the anomalous charging current, the permanent flow being assumed to be the true conduction current. This identity is rendered doubtful, however, by observations made on other substances by several experimenters, who find that the permanent current is not proportional to the potential difference.

Saegusa also examined the effect of changing temperature on the reversible dielectric anomalies, in the range 7 to 27°C. The time necessary to attain the steady state is shortened by increased temperature. The quantitative results, however, are open to question, because nearly all the curves show inflections in the region 14 to 18°C. No inversion or unusual change in quartz is known at these temperatures, and the form of the curves therefore strongly suggests a temperature effect upon some concealed error, brought out by a departure in either direction from 17°, which is the temperature at which most of the measurements were made.

Curtis.—Curtis [10] measured the delayed discharge in quartz by his direct-current method, already described (method (1) p. 519). With a charging time of 0.5 second and a momentary discharge 0.05 second later, there is a delayed discharge at the end of 0.5 second amounting to 11 per cent of the original charge, and after 1 second, to 13 per cent.

The resistance was measured by a leakage method and found to be 69×10^{12} ohms, but the direction was unfortunately not recorded.

Shaposhnikov.—Shaposhnikov [11] found that the current in quartz in the direction of the axis follows Ohm's Law only for values of potential difference below 400 volts per mm and for short durations of flow. At higher voltages or for longer times of flow the departure increases with both voltage and time.

A comparison of measured resistivities follows. It is assumed that Curtis' is parallel to the axis, which seems probable from its order of magnitude.

Observer	R in ohms	
	Quartz ∥ to axis	Quartz ⊥ to axis
Thornton	0.15×10^{15}	20×10^{15}
Richardson	0.02×10^{15}	4.3×10^{15}
Curtis	0.07×10^{15}	

[9] Saegusa, H., Sci. Rep. Tohoku Imp. Univ., First Series (1921) **10**: 437-443, 13 pls.

[10] Curtis, H. L., article cited in XXVI, note [4].

[11] Shaposhnikov, A., J. Russian Phys.-Chem. Soc., Phys. Sect. (1910) **42**: 376-400.

Measurements at 100 *to* 500°C

Ambronn.—The most extensive piece of work on the conductivity of quartz done in recent years is that of Ambronn.[12] He measured the current which flowed through plates of quartz between silvered copper electrodes with applied constant voltages of 0.006 to 10.5 volts, at temperatures where the current was measurable by means of a galvanometer, namely, 166 to 466°C. 82 series, involving about 4000 individual measurements, were made on 15 plates of quartz cut at different angles to the axis. All but one of these plates were cut from a single crystal.

Good electric contact was secured by chemically platinizing the faces of the plates. In order to avoid the rapid fall of conductivity, due partly at least to electrolysis, when a direct constant current is used, the current was rendered alternating in the specimen itself by means of a rotating commutator yielding frequencies of 1 to 130 per second.

It was found that the frequency of the alternations has a large influence on the measured resistance, the apparent resistance increasing as the frequency decreases. This variation is similar in form for all the specimens, even though their actual resistivities may be very different, which makes it possible to express analytically the relation between frequency and resistance and to extrapolate to infinite frequency (or zero period).

The relation is

$$R = R_0 + aP^{\frac{1}{2}}$$

where R is the measured resistance for alternations of period P, R_0 is the resistance at zero period, and a is a constant.

The applied voltage also has an effect on the measured resistance, the resistance appearing smaller, the higher the voltage. The effect is small compared with that of frequency, and it becomes smaller with increase of frequency, so that with the assignment of a little extra weight to the high-frequency measurements the effect may be disregarded in the analytical expression.

The relation of R_0 to temperature may then be considered independently of the conditions of measurement. It is best expressed by the formula

$$R_0 = Ae^{\frac{B}{T-C}}$$

where T is the absolute temperature and A, B, and C are constants. The temperature coefficient of resistance is determined by the constants B and C, while the actual value of the resistance, involving the form and orientation of the plates, is determined by A.

Evaluation of the constants shows that the various series are in good agreement in assigning to C the value 224.9 ± 2.3. Physically interpreted, this means that the conductivity would become zero at the temperature 225°K or —48°C.

Agreement is not so good on the value of B, which varies between 1413 and 1586. Apparently there is a real variation in the temperature coefficient,

[12] Ambronn, R., *Untersuchungen über die elektrische Leitfähigkeit des Bergkristalles*, Dissert., Göttingen, 1913. Verh. Kais. Leopold.-Carol. Deut. Akad. Naturf. Halle, 1915, 101: 177-268, pls. 30-38.

explainable by inhomogeneity in the character and distribution of the conducting material of the crystal.

The values of A can be rendered consistent only on the principle that conduction in a quartz crystal follows strictly the direction of the optic axis. If the plate is of such dimensions and is oriented in such a way that no lines parallel to the axis cut both electrodes, then the resistance is too high to measure by Ambronn's method. The results thus furnish a more ample basis of fact for the observations of earlier observers that plates perpendicular to the axis conduct many times better than plates parallel to the axis.

TABLE XXVII.4.

CONDUCTIVITY OF QUARTZ. J. CURIE, 1888.

Constants in the formula $L = aZ^n$. L in c.g.s. electrostatic units per sq. cm per cm.

Description of specimen	Temperature °C	Conductivity in direction of axis		
		$10^5 a$	n	Period over which formula was verified
Plate No. 2	7	8.1	0.0216	1 min. to 3 days
" No. 3	7	23.1	0.285	20 sec. to 3 hours
" No. 4	7	3.37	0.145	1 min. to 2 days
" No. 5	7	5.71	0.278	1 min. to 3 hours
" No. 6	20	16.88	0.167	10 sec. to 1 hour
" No. 7	20	60.3	0.286	1 min. to 11 days
0.5 mm plate.....	100	450	0.525	10 sec. to 10 min.
" " "	140	10,800	0.52	10 sec. to 16 min.
" " "	200	246,000	0.72	10 sec. to 3 hours
15 mm cylinder.....	250	955,000	0.11	30 sec. to 1 hour
" " "	300	32,400,000	0.16	30 sec. to 1 hour
		Conductivity perpendicular to axis		
	20	1.12	0.907	40 sec. to extinction
	100	0.229	0.3	60 sec. to 3 hours
	160	2.61	0.06	40 sec. to 1 hour

Nearly 400 additional observations were made on 2 quartz plates cut perpendicular to the axis, at 228 to 460°C, using a commutator to give alternately a charge at a constant voltage of 0.05 to 60 volts, and a discharge through a galvanometer. It was found that the apparent polarization e. m. f. produced in such plates may exceed by many fold the e. m. f.'s obtainable in liquid electrolytes. The extrapolated e. m. f. at infinite frequency of alternations (zero period) is nearly independent of temperature and is always in the same ratio to the applied voltage. Results entirely free from the effect of a high-resistance anode layer could not, however, be obtained.

Curie.—The striking difference between the axial and equatorial conductivities of quartz was first reported by J. Curie [23] in 1886, but full details were not published until 1888.[24]

Curie made a study of the electric conductivity of quartz as part of a gen-

[23] CURIE, JACQUES, Compt. rend. Acad. Paris (1886) **103**: 928-931.

[24] CURIE, J., Thesis cited in XXVI, note [2]. Also Ann. Chim. et Phys. (1889) (6) **18**: 203-269.

eral investigation on the conductivity of crystalline insulators. He measured the flow of electricity by balancing it against the output of a "piezo-quartz" plate (see p. 561). The conductivity was measured of 7 plates cut perpendicular to the axis, and several others parallel to the axis, at temperatures from 7 to 300°C. The effect of prolonged heating at various temperatures was also examined.

The results are expressed in the form of apparent conductivity per sq. cm per cm, that is, the ratio of current to voltage at any instant. Ohm's Law of the proportionality of current to applied voltage was found to hold strictly for the range of voltage used, namely 1 to 300 volts, and the apparent conductance was also found proportional to the thickness of the plates. (The limits are not stated, but appear to have been of the order of 0.5 to 15 mm.)

An important experimental principle independently discovered by Curie in his measurements on quartz, but originally announced by Hopkinson (1876), is the *law of superposition.* The law states that "Each variation of the electromotive force between the two faces of the plate acts as if it were alone." This means that the current observed at any instant is the algebraic sum of the currents which would have been produced at this instant by each applied voltage acting alone from its time of application. A reduction of the applied voltage, for example, is equivalent to the application of a new voltage of opposite sign and equal to the amount of the reduction. The law gives a simpler statement of the relation of charge and discharge currents than is given by the assumption of a counter e. m. f.

In every case the apparent conductivity of quartz was found to diminish with time of flow of the current, following, after the first minute of rapid change, a course expressed by the formula: $L = aZ^{-n}$, where L is conductivity, Z is time, and a and n are constants. This decrease was observed for various periods up to a maximum of 11 days.

Values of these constants as determined by Curie are given in Table XXVII.4.

Tegetmeier & Warburg.—Before J. Curie's detailed results had appeared, an experimental study of the axial and equatorial conductivities of quartz had been begun by Tegetmeier & Warburg.[25] They measured the current produced by direct voltages of 19 to 1600 volts applied by way of platinum electrodes to the gold-leaf-plated faces of clear homogeneous quartz plates 5×15 mm, heated in an air bath at various temperatures up to 300°. 5 plates perpendicular to the axis and 3 parallel thereto were used.

Further experiments,[26] in which the electrodes were metal cups which could be filled with mercury or amalgam, demonstrated clearly that the axial conductivity is electrolytic in character. This is shown by the following facts:

(1) When sodium amalgam is used as anode and mercury as cathode, at about 230°C, the conductivity remains constant, and a quantity of sodium chemically equivalent to the current which has passed, within 2 per cent, is found in the mercury.

[25] Tegetmeier, F., & Warburg, E., *Ueber eine besondere Art von electrischer Polarisation in Krystallen,* Ann. Phys. u. Chem. (Wiedemann) (1887) **32**: 442-451.

[26] Warburg, E., & Tegetmeier, F., *Ueber die electrolytische Leitung des Bergkrystalles,* Ann. Phys. u. Chem. (1888) **35**: 455-467.

(2) The quartz which served for the foregoing experiment left a residue of 0.050 per cent of a soluble sulfate, when dissolved in pure HF and H_2SO_4.

(3) When pure mercury or gold are used as electrodes the conductivity falls off rapidly as the current continues to flow.

(4) If after such an experiment the applied voltage is reversed, the conductivity is partly restored before it again diminishes.

(5) The conductivity of a specimen whose conductivity has been lowered by the passage of current is not affected by the cutting away of layers from the cathode side, but is brought back toward its original value when layers are cut away from the anode side.

(6) The optical and "pyroelectric" (piezo-electric) properties of quartz undergo no observable change as the result of the passage of current.

(7) The combination mercury ‖ quartz ‖ sodium-amalgam acts as a galvanic cell and gives a voltage of 1.3 to 2 volts at 225°C.

The following additional facts concerning the axial conductivity were brought out by Warburg & Tegetmeier's experiments:

When potassium amalgam is used as anode, the conductivity falls off as when pure mercury is used, and no potassium is found at the cathode.

The axial resistivity of quartz at 224°C is 20 to 70 megohms, for potential differences of 200 to 300 volts per mm. The axial conductivity of quartz at 224° is therefore nearly the same as that of soft soda glass at the same temperature, as measured by Beetz. The resistance at high potential differences is always smaller than at low. It increases with time if the p. d. has been lowered from a previously higher value, and, vice versa, it decreases with time if the p.d has been raised from a previously lower value; as if a definite value of resistance corresponded to each value of current strength, and the measured resistance tended to approach this value if the current were held constant.

TABLE XXVII.5.

ELECTRIC RESISTIVITY OF SILICA. F. M. EXNER, 1901.

Temp. t	Resistivity Ohms × 10^9	Remarks
	QUARTZ, DIRECTION ‖ TO AXIS.	
148	0.22	Voltage 240 v. Thickness of plate 4 mm. Electrodes of sodium amalgam.
126	0.94	
109	4.7	
148	0.22	
	VITREOUS SILICA (Schott & Gen.).	
101.0	390	Voltage 240 v. Thickness of plate 9 mm. Electrodes of sodium amalgam.
124.5	210	
147.0	80	
151	370	Electrodes of mercury.
122	1400	
106	2450	
156	700	

Tegetmeier & Warburg also observed the principal features of the "polarization" phenomena, namely: the rapid fall of a direct current from a high initial value; the production of a current in the reverse direction; and the high polarization voltage, exceeding 150 volts, which shows that the phenomenon is not due entirely, if at all, to the familiar electrolytic e. m. f. This apparent high polarization is probably one of the results of the reversible anomalous charging current (p. 526).

Exner [17] measured the resistance of a plate of quartz, cut perpendicular to the axis, and a plate of vitreous silica, at temperatures of 100 to 150°C. He used Warburg & Tegetmeier's type of apparatus with liquid electrodes. The results are given in Table XXVII.5.

Curie [18] observed that the conductivity of plates of quartz cut perpendicular

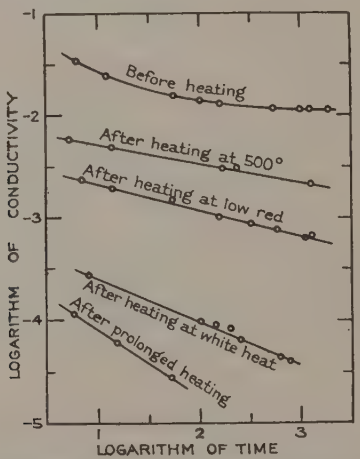


FIG. XXVII.4.—Conductivities at 20° of a plate of quartz which has been heated to high temperatures. J. Curie, 1888.

to the axis decreased considerably as a result of their being heated to various temperatures from 500° to a "bluish white" heat. The relation of conductivity and time of flow of current in such a plate which has been heated to successively higher temperatures is illustrated in Figure XXVII.4.

The final heating lowered the conductivity to a value which was barely measurable. The constitution of the specimen remained unchanged, however, as shown by the fact that the optical rotatory power for yellow light of one such plate was 21.67 degrees.

Soaking in cold water, and heating with water in a sealed tube for an hour at 250°, failed to restore the lost conductivity of heated plates.

The heating of plates cut parallel to the axis, on the other hand, did not

[17] EXNER, F. M., *Zur inneren Leitung von Quarz bei 100-150° und von Glas bei Zimmertemperatur*, Verh. Deut. Phys. Ges. (1901) 3: 26-30.

[18] CURIE, J., article cited in note [14].

affect their conductivity, as measured in the direction perpendicular to the axis (equatorial conductivity).

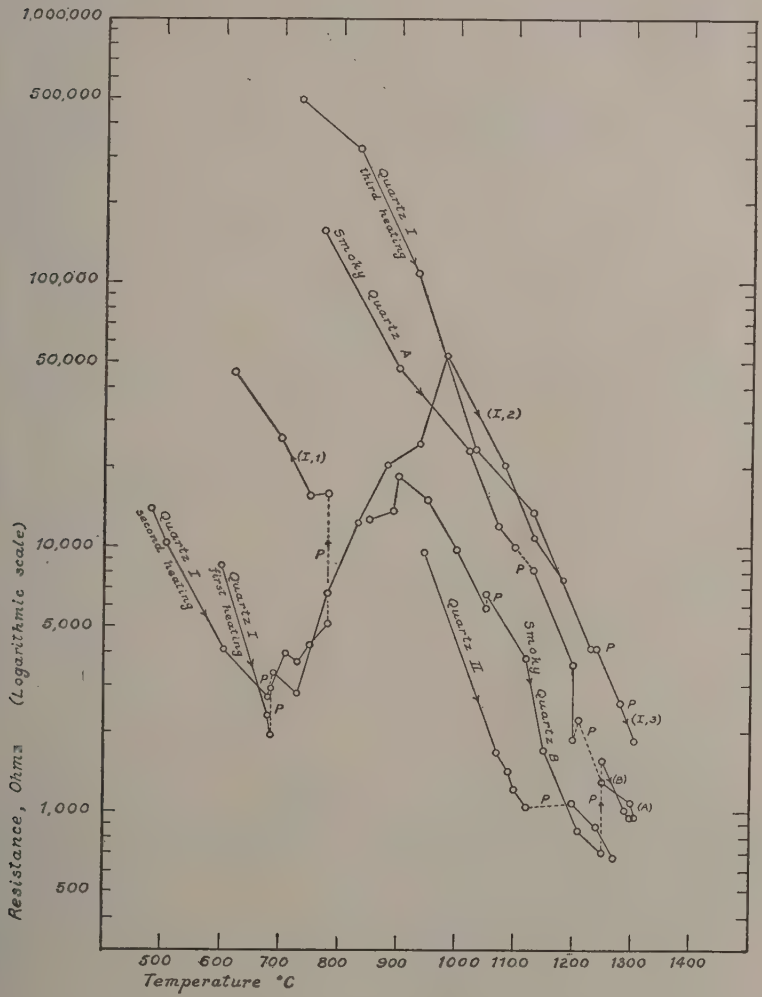


FIG. XXVII.5.—Data on the change of electric resistance of quartz with temperature, in the direction parallel to the axis. (Resistance of plates 1 × 10 × 10 mm, cut perpendicular to axis, electrodes against flat sides. Straight lines connect the successive measurements in each series. Dotted line or letter *P* signifies that a polarization test, involving passage of a direct current for 10 to 30 minutes, was made between the temperatures indicated. Measurements by Doelter, 1908.)

Measurements above 500°

Doelter [19] has carried the measurements of the electric conductivity of silica to higher temperatures than any other investigator. He used plates of vitreous silica and of quartz cut parallel and perpendicular to the axis, of dimensions $1 \times 10 \times 10$ mm, gold-plated, and compressed between electrodes of platinum. The resistance was measured by means of a Wheatstone bridge, with high-frequency alternating current from an induction coil, settings being made with the aid of a telephone. The method is not well suited for very high resistances, and satisfactory measurements were therefore not obtained below about 600 to 900°.

I have plotted the original published data in Figures XXVII.5 and 6, in order to make a graphic comparison of the results obtained with different specimens.

Figure XXVII.5 contains the data on plates cut perpendicular to the axis, and therefore yielding conductivities in the direction of the axis. The values are the measured resistances of the 1-mm plates. Neither the resistances nor the temperatures are precise and there is no need of tabulating the data. At intervals in the course of the measurements "polarization tests" were made, involving the passage of a direct current through the plate with a voltage of 140 to 190 volts.

These currents, as well as repeated heatings of the plate, have large effects, as is evident from Figure XXVII.5. Each reheating of quartz specimen I, and in most cases each passage of direct current through it, shifts its resistance toward higher values. The final curve forms a kind of envelope of the group, representing a state toward which the other curves tend. It is as if some conducting substance were being electrolyzed and volatilized out of the plates.

The data on resistivity $\perp$ to the axis, shown in Figure XXVII.6, are qualitatively in agreement with the results of Curie, of Warburg & Tegetmeier, and of others already referred to. The resistance is higher than in the specimens of Figure XXVII.5, in which the current flowed $\parallel$ to the axis. Furthermore, the effect of heating and of direct-current electrolysis is less, as if whatever conducting impurity was present was taking a less important part in the conduction.

In connection with these measurements of the electric conductivity of silica Doelter also tested qualitatively the polarization phenomena. A steady voltage of 140 to 190 volts was applied during 10 to 30 minutes, and the current which flowed was measured with a milliammeter. The "discharge" through a shunted galvanometer was then measured, beginning just after this charging voltage had been disconnected.

The charging current under these conditions was found to increase with the temperature, being from 0.5 to 2.7 milliamperes. The discharge current likewise increased with the temperature, and was of the order of 0.001 to 0.01 milliampere. This current fell off in 5 or 10 minutes either to zero or to a constant current which was thought to be of thermo-electric origin.

[19] Doelter, C., *Über die elektrische Leitfähigkeit fester Silikate*, Sitzungsb. Kais. Akad. Wiss. Wien, Math.-Nat. Kl. (1908) **117, I**: 845-874. *Die Elektrizitätsleitung in Krystallen bei hohen Temperaturen*, same (1910) **119, I**: 49-111. Also in *Handbuch d. Mineralchemie* (1914, Dresden) **II, 1,** pp. 115-157.

The polarization effects with vitreous silica were smaller than they were with quartz in the direction perpendicular to the axis.

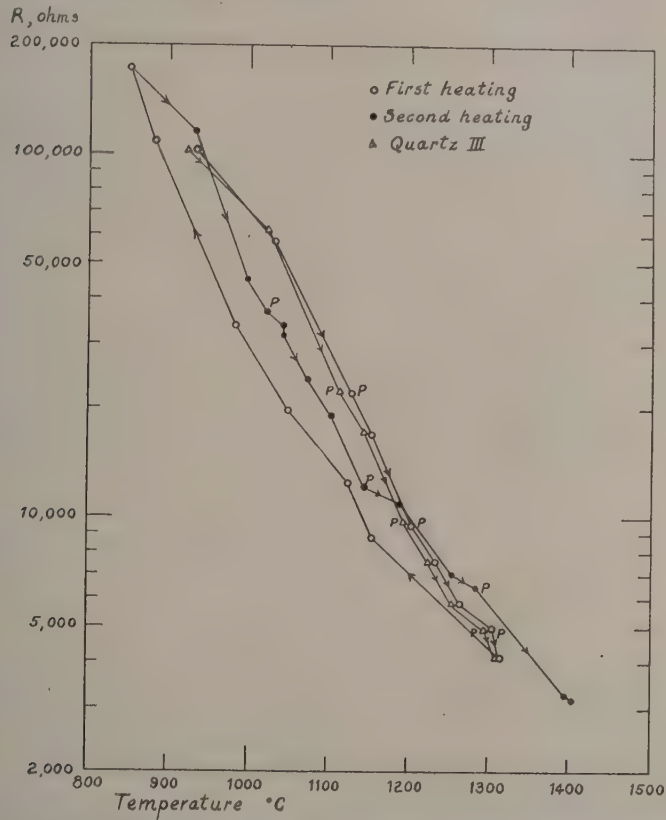


FIG. XXVII.6.—Data on the change of electric resistance of quartz with temperature, in the direction perpendicular to the axis. (Resistance of plates $1 \times 10 \times 10$ mm, cut parallel to the axis, electrodes against flat sides. Straight lines connect the successive measurements in each series. Letter *P* signifies a polarization test; see Figure XXVII.5. Measurements by Doelter, 1908 and 1910.)

THE EXPERIMENTAL DATA ON STORAGE AND FLOW OF ELECTRICITY IN VITREOUS SILICA

Attention was especially drawn to the excellent insulating power of vitreous silica by Boys [20] in 1889, who showed that rods of it insulated the charge on a pair of gold-leaves about 11 times as well as soda glass

[20] Boys, C. V., Proc. Physical Soc. Lond. (1889) **10**: 128-132.

in dry air, and that its insulating power was not affected by moist air or even by dipping the rod in distilled water and allowing it to remain wet. It was also unaffected by washing in solutions of KOH or HCl, but two minutes' immersion in melted potash, followed by washing, somewhat impaired the insulating power, which was not restored by boiling in strong HCl solution.

More exact quantitative data on the currents in vitreous silica at room temperature were lacking until the publication of Thornton's measurements (1910). These have been followed by data from Curtis (1915), Jaquerod & Capt (1916), Jaquerod & Mugeli (1922), and Bush & Connell (1922).

At higher temperatures there are measurements by Exner (1901), Horton (1906), Doelter (1908), Pirani & Siemens (1909), Campbell (1910), and Silsbee, Honaman, & Fonseca (1919).

Jaquerod and associates.—As a result of more than 200 measurements of the anomalous charge and discharge currents in vitreous silica, Jaquerod & Mugeli [21] reached the following conclusions:

(1) The empirical formula: $y(Z) = BZ^{-n}$, with which most experimenters have been able to represent the anomalous current, is found insufficient, and has to be replaced by the empirical formula:

$$y(Z) = Ae^{-\alpha Z} + Be^{-\beta Z} + Ce^{-\gamma Z}$$

From this it follows that the quantity of electricity transported by the residual current is

$$Q_0^{\infty} = \int_0^{\infty} y(Z)\,dZ = \frac{A}{\alpha} + \frac{B}{\beta} + \frac{C}{\gamma}$$

(2) A normal conduction current is observed at temperatures of 60 to 100°.

(3) The residual charge and discharge currents are not in most cases superposable, as they are supposed to be under the theory of Hopkinson, and as they were actually found to be in quartz by J. Curie (see p. 538). The principle of superposition must be generalized thus: "The total quantity of electricity transported by the anomalous discharge current is equal to that transported by the anomalous charging current." The superposability of the curves themselves is of course a special case of this more general statement.

(4) The quantity of electricity transported by the anomalous current is a function of the temperature and of the previous thermal history of the specimen.

Rising temperature alone has the effect of producing a rapid decrease of the anomalous current. Between 20° and 65° the quantity of electricity transported is represented by: $Q = Q_0 e^{-0.0765t}$.

From preliminary measurements it appears that in the empirical equation $y(Z) = Ae^{-\alpha Z} + Be^{-\beta Z} + Ce^{-\gamma Z}$ only the quantity α increases with the temperature, while β and γ remain practically constant.

[21] JAQUEROD, A., & MUGELI, H., *Recherches sur les anomalies diélectriques du verre de silice,* Arch. sci. phys. nat. (1922) (5) **4**: 10-26, 89-119.

The temperature also has a considerable permanent influence on the dielectric properties, an influence which has not been quantitatively defined. It depends not only upon the temperature itself, but also upon the time during which the glass has been at the given temperature.

(5) Under the influence of certain causes, still unknown, the anomalous current varies in a capricious fashion from day to day. These variations are sometimes considerable and the current may be double or even treble what it was at some previous date. These effects have not been found explainable either by the temperature, or by the action of radioactive substances.

(6) Dissolved gases have been found to have an effect on the anomalous

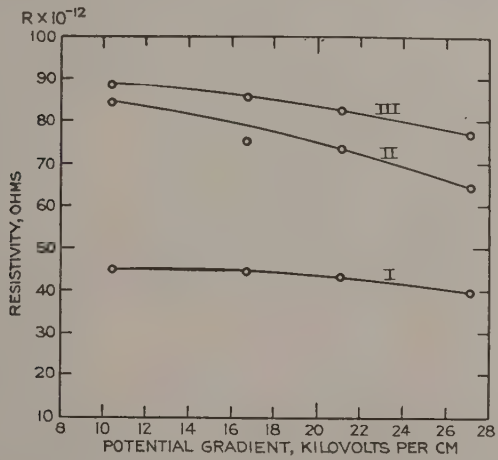


FIG. XXVII.7.—Electric resistivity of vitreous silica at 25.0°C, as influenced by the removal of gases by heating. Bush & Connell, 1922.

Curve I. Specimen in original state.
Curve II. After evacuation at 350°C.
Curve III. After re-exposure to air for 2 days.

charge and discharge currents. A vacuum also has an effect. No quantitative relations have been found.

The existence of such effects due to gases was shown by the preliminary experiments of Jaquerod & Capt,[22] but further experiments by Jaquerod & Mugeli have failed to make the relations any clearer.

Thornton.—Thornton's method has already been described. He found that the rate of polarization in an ellipsoid of vitreous silica freely suspended in the field is much more rapid than in quartz, the value becoming steady in about half an hour and remaining unchanged after several days in the field. The apparent resistivity rose from 0.71×10^{15} ohms per sq. cm per cm at 0.5 minute to 11.5×10^{15} at 25 minutes.

Curtis.—Curtis [23] measured the resistance of a flat plate of vitreous silica

[22] JAQUEROD, A., & CAPT, C., Arch. sci. phys. nat. (1916) (4) **42**: 328.
[23] CURTIS, H. L., Bull. Bur. Standards (1915) **11**: 359-420. (Sci. Paper 234.)

floating in mercury at room temperature, using a constant voltage of about 200, and measuring the current with an electrometer.

The current through the specimen diminished steadily until the apparent resistivity became too high to measure, namely, over 5000×10^{15} ohms per sq. cm per cm after 18 hours. The measured progressive change with time was from about 40×10^{15} at the start to about 2000×10^{15} after an hour.

Bush & Connell.—Bush & Connell[24] have recently determined the effect of removing absorbed gas upon the electric conductivity of transparent[25] vitreous silica. Figure XXVII.7 shows the results. The specimen was in the form of a tube about 1.6×10 cm, closed at one end. The electrodes consisted of copper plated on to the glass, inside and out. Direct constant potential from a generator was used. Measurements were first made on the tube after it had been washed in ether and dried in warm air. The specimen tube and its inclosing tube were then evacuated with a Langmuir pump and heated at 350°C until no more gas was evolved; after cooling in vacuum, a second set of measurements was made. Atmospheric air was then admitted and further tests made.

Single measurements on the vitreous silica tube made during 2 months all fell between curves II and III in Figure XXVII.7.

Pyrex glass and Corning glass G-702 reabsorbed material from the atmosphere after similar treatment and decreased in resistivity toward their original values. Vitreous silica did not show this effect.

The active agent is probably water, which forms most of the gas extracted from glasses by heating in vacuum.

Surface resistivity

The "surface resistivity" of an insulator, defined as the actual resistance between the opposite edges of a surface 1 cm square, depends almost entirely upon the humidity of the surrounding air. It is due to a surface film, usually of water or oil. The current transmitted by a fragment of a good insulator such as quartz or vitreous silica at room temperature may be carried almost entirely by the surface film and scarcely at all through the body of the substance, and account must be taken of this fact in all experimental determinations of the resistivity.

Surface resistivities of vitreous silica as measured by Curtis[26] are shown in Figure XXVII.8. For curve I the specimen was simply wiped with a cloth. For curve II it was further cleaned by means of strong chromic acid, washed, and dried. The higher resistance is probably due to the absence of any soluble impurities in the surface film of moisture.

High-temperature data on vitreous silica

The high-temperature data have been chiefly measurements of the theoretically constant resistivity in Ohm's Law. But, as already shown

[24] Bush, V., & Connell, L. H., J. Franklin Inst. (1922) **194**: 231-240.
[25] According to correspondence with Prof. Bush.
[26] Article just cited.

for quartz, the relation between current and voltage usually deviates from the constancy called for by Ohm's Law, and the time of flow becomes an important factor. Results with alternating and with direct current may therefore be expected to differ.

Some of the high-temperature data are compared in Figure XXVII.9.

Horton[27] measured the resistance of a slab of vitreous silica about $9 \times 9 \times 1.5$ mm in dimensions, platinized chemically on both faces and pressed

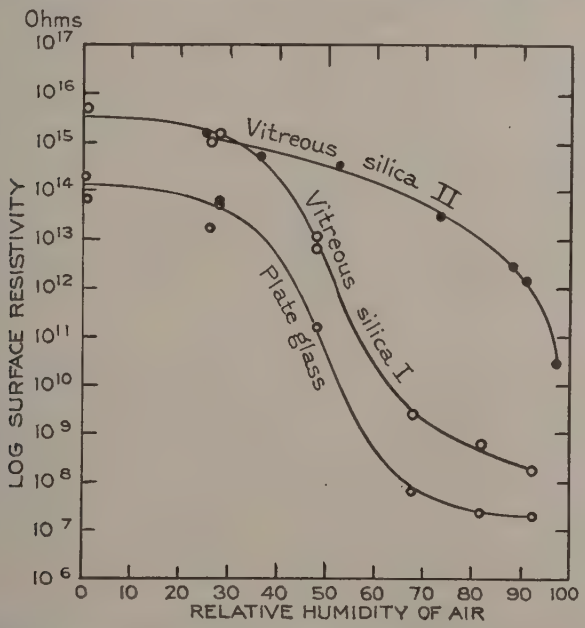


FIG. XXVII.8.—Surface resistivity of vitreous silica as affected by air humidity. Curtis, 1914.

between platinum electrodes. The resistance was measured by the Wheatstone bridge method, the observer noting only the initial direction of movement of the galvanometer and reversing the current at each test, to avoid the so-called "polarization" or anomalous effects. Measurements were made at 11 temperatures between 486 and 1288°C.

Campbell[28] measured the electrical resistance through the walls of tubes of silky-surfaced vitreous silica made by the Thermal Syndicate. The voltage was 200 to 500 volts, and the resistance was measured after 1 minute of flow

[27] HORTON, F., *The electrical conductivity of metallic oxides*, Phil. Mag. (1906) (6) **11**: 505-531.

[28] CAMPBELL, A., Proc. Physical Soc. Lond. (1913) **25**: 336-337.

of current. This method does not give as precise or accurate results as the cup method used by Silsbee.

Doelter's measurements were made with alternating current by the method already described (p. 542). His results are included in Figure XXVII.9, shown in the same manner as his data on quartz.

Silsbee, Honaman, & Fonseca tested the electrical resistance of vitreous silica incidentally to a series of experiments on the electrical properties of gasoline-engine spark-plugs.[29]

The tests were made on a crucible and two tubes [30] between about 480 and about 830° [31] While the data confirm the general character of the change in resistivity indicated by the curves of Figure XXVII.9, the dimensions of the specimens are not sufficiently well defined to yield accurate values for R, although they do show that vitreous silica has a resistivity far higher than that of Pyrex glass, and also clearly higher than that of most porcelains.

Pirani & Siemens [32] made measurements by means of alternating current with bridge and telephone, at 8 temperatures between 899 and 1261°C, on a tube of vitreous silica [33] held between carbon electrodes. The resistance of the tube was found to follow the law: $\log R = a + b/T$, in which a and b are constants and T is the absolute temperature. The resistivity was approximately 40,000 ohms per sq. cm per cm at 1000°K (727°C). This is the lowest of the recorded values for vitreous silica in this region of temperature.

General features

Looking over the results, as a whole, on the storage and flow of electricity in silica, it seems to me that what is most needed for the sake of bringing order into the chaos is the services of a chemist. How many, and which, of the specimens investigated were reproducible material? It is impossible to say. Certainly the data on *axial* conductivity of quartz are, in the absence of chemical control, without meaning so far as the properties of quartz itself are concerned. The same may be in part true for the conductivity of vitreous silica and the equatorial conductivity of quartz.

On the physical side a promising approach has recently been made by Addenbrooke,[34] who has proposed a useful method of determining and representing the dielectric properties of an insulator such as silica. The substance is made the dielectric of a condenser in a circuit in which the potential and the alternating potential difference are kept the same but the frequency is varied from 1 to 2000 or more per second. The readings of a voltmeter and an ammeter show the amount of energy circulating in the circuit, and give its value by their product. At the same time a sensitive electrostatic wattmeter meas-

[29] Silsbee, F. B., & Honaman, R. K., Nat. Advis. Com. Aeronautics, 5th Ann. Rep. (1919) 79-89 (Report 53, I).
[30] Honaman, R. K., & Fonseca, E. L., Same, pp. 91-99 (Report 53, II).
[31] According to information from Dr. Silsbee.
[32] Pirani, M. v., & Siemens, W. v., Zeitschr. Electrochem. (1909) **15**: 969-973.
[33] Referred to in original as "Quarz."
[34] Addenbrooke, G. L., Nature (1924) **113**: 490-491.

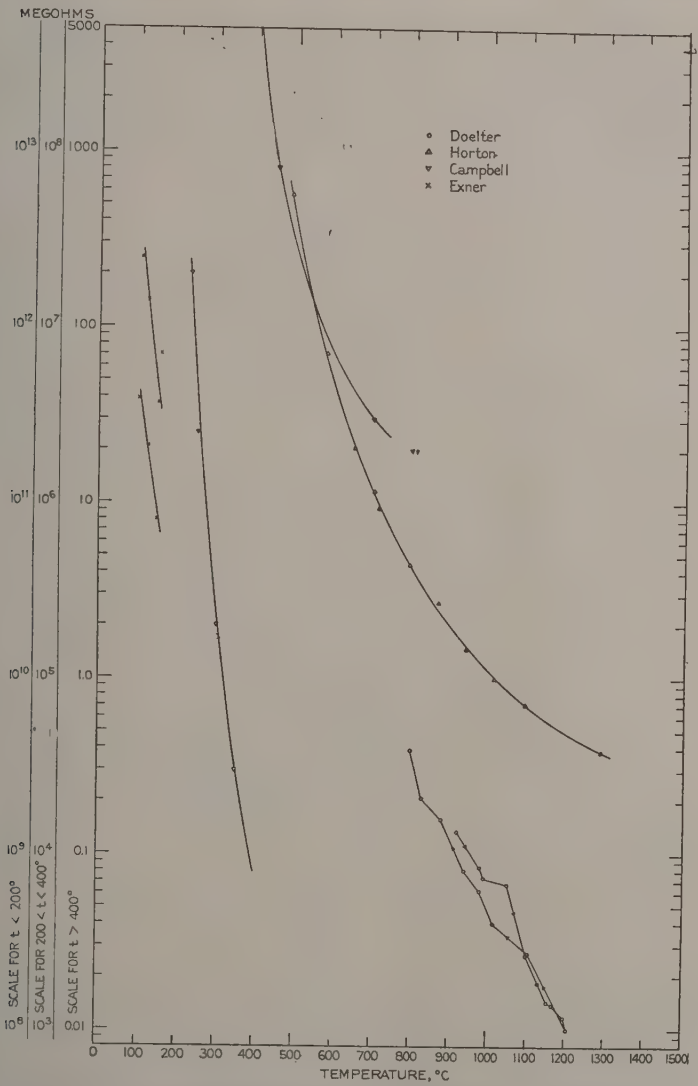


FIG. XXVII.9.—Experimental data on the resistivity of vitreous silica at high temperatures.

ures the energy d which is dissipated in the dielectric and converted into heat. The "reversible energy" r, proportional to the pure charge and discharge at each alternation, can then be calculated: $r^2 = IE^2 - d^2$, where I is the current and E the potential difference. The dimensions of the condenser being known, the pure dielectric constant, which applies only to the strictly reversible part of the charge, can be calculated for each frequency.

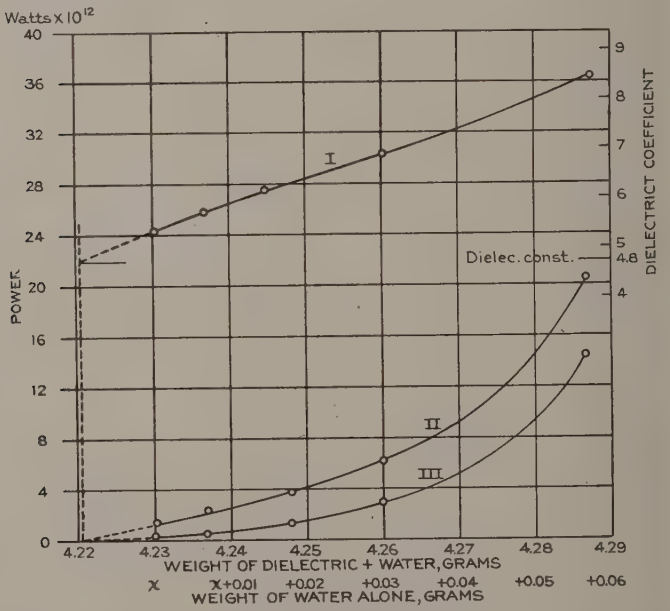


FIG. XXVII.10.—Variation of the reversible and the dissipated energy with water content in celluloid. Addenbrooke, 1924.

Curve I. Reversible energy at 8 cycles per second (capacity).
Curve II. Energy dissipated at 8 cycles per second.
Curve III. Energy dissipated at constant potential.

Measurements of this kind were made on sheet celluloid. Above a frequency of 1000 cycles its dielectric constant is very nearly independent of frequency and has a value of about 6.56 at 2000 cycles. Two important facts are brought out: (1) the curve of dissipated energy has the same form as that of the reversible energy, and (2) the proportion of dissipated energy grows larger at lower frequencies.

Although measurements of this kind have not been made on silica, the known dielectric phenomena of quartz and vitreous silica would fit into a pair of curves such as those for celluloid, as shown in the original paper.

Now comes the interesting part of the celluloid investigation for the sake of which it is introduced here.

If the celluloid be dried thoroughly and measurements similar to those just described be made in air whose moisture content is controlled, the data shown in Figure XXVII.10 are obtained. A specimen of celluloid was dried as thoroughly as possible by warming in a vacuum. The dielectric constant had the value 4.8 and was practically independent of frequency, as proved by tests from 8 to 200 cycles; also its resistance was increased about 100 times. Another specimen was dried in air at 100°, and its reabsorption of water was controlled by the admission of small amounts of moist air. This gave the curves of Figure XXVII.10, starting with the unknown residual percentage marked "*x*." The combination of these data in the figure indicates that the second specimen started with a content of about 0.01 gram of water, and that when completely free from water its "dielectric hysteresis" would be practically zero.

Furthermore, the dielectric constant of the completely dry celluloid is nearly independent of temperature, while the dielectric constant and the dissipated energy of celluloid containing moisture have large temperature coefficients.

In several ways the electric properties of quartz resemble those of celluloid. It has appreciable dielectric after-effects varying from one specimen to another. Its conductivity is measurable, and likewise variable from specimen to specimen. Its conductivity increases rapidly with rising temperature. When quartz is heated for a time its conductivity falls considerably.

There is evidence from other directions that natural quartz crystals contain small amounts of water and probably other impurities. It is reasonable to expect that if these impurities could be removed the axial conductivity of quartz would fall to a value near to its transverse conductivity and also approaching that of vitreous silica. At the same time its dielectric constant would diminish and would become more nearly the same from specimen to specimen.

The large electrical effect of very small amounts of such impurities is evident from Addenbrooke's experiments, which show that a change of 0.001 per cent in the moisture content of celluloid produces a measurable effect.

The differences in the piezo-electric constant of quartz, which mystified Röntgen, may perhaps also be traced to the same impurities (see XXVIII).

Hypotheses on the axial conductivity of quartz

The discoveries of J. Curie and of Tegetmeier & Warburg concerning the unusual character of the axial conductivity of quartz naturally aroused much interest among physicists and mineralogists, and several different hypotheses were put forward to explain the facts. Curie thought that the results could be explained by the assumption that there are channels of molecular size, parallel to the axis, filled with water and possibly other substances, and he made a series of experiments on porcelain and other water-absorbing materials, both when wet and when dry, tending to show that the phenomena in quartz are of the same character.

Tegetmeier & Warburg ascribed no importance to the presence of

water, but considered that the sodium which they showed was the active agent in the conductivity is present in the form of Na_2SiO_3 which, as they express it, "takes a part in the structure of the crystal," a relation which we would now call "solid solution." The process of conduction would then be similar to conduction in soft glass as studied by Warburg, namely, a movement of sodium toward the cathode while the SiO_3 remains fixed. This can hardly be a complete statement because oxygen must be released somewhere unless we are to suppose that it remains dissolved or forms a higher oxide of silicon.

The strictly axial character of the conductivity requires that this solid solution be of rather unusual type. According to Clausius' theory of electrolytic conduction there is movement of ions and interchange of electricity between molecules at all times even if no potential difference is acting. In quartz this movement and interchange must occur only in the axial direction.

In reviewing the two papers of Tegetmeier & Warburg, Beckenkamp [35] adhered rather to Curie's view, considering that water is the active agent, but suggesting sodium chloride as the substance which makes the water conducting. The hypothesis is supported by the fact that salt solutions are frequently found in quartz in the form of liquid inclusions. The solutions responsible for the axial conductivity are supposed, however, to be uniformly and very intimately distributed throughout the body of the quartz, perhaps intramolecularly, in much the same manner as the ultramicroscopic substances which cause the brown color of smoky quartz. Beckenkamp showed that the quantities of sodium salt which Tegetmeier & Warburg had found in the hydrofluoric acid residue from quartz crystals, if uniformly distributed in water to the dilution in which they exist in quartz, would give the water a conductivity about 100,000 times greater than that possessed by the quartz. The amount of salt must then be very much less than the quantity indicated by the analysis, or, what seems more likely, its conductivity in the crystal is limited by the very narrow space in which it is permitted to move,—a space so narrow that sodium is about the largest atom which can pass through, experiment having shown that potassium can not be made to enter.

The three views may be thrown into contrast by the following tabulation:

	Structure	Active Agent
Curie	Heterogeneous	Water
Warburg & Tegetmeier	Homogeneous	Sodium
Beckenkamp	Homogeneous	Water

Theory of the dielectric anomalies in silica

Maxwell showed clearly in 1873 how the reversible anomalous current can be accounted for by the assumption of a layered dielectric,—one which

[35] Zeitschr. Kryst. (1889) **15**: 511-516.

is made up of plane-parallel sheets differing in dielectric constant and in conductivity but possessing in themselves no anomalies of electric behavior. The principle of superposition (p. 538) is a direct consequence. The assumption of such a structure seems to have been accepted by some as a satisfactory explanation of the reversible phenomena in quartz, especially since the assumption is supported by the known habit of polysynthetic twinning in thin laminae which is characteristic of amethystine quartz. In view of our present knowledge of the structure of untwinned quartz (see XIII and XIV), however, the explanation can not be accepted.

The reversible anomalies are better explained by some type of theory involving an anomaly in the dielectric displacement itself, probably a dielectric after-effect depending on the time and analogous to the elastic after-effect (see p. 451). The electric units concerned may be molecular dipoles of the kind assumed in current hypotheses of the structure of solids.

Looking at the problem in another way, we may picture the movement of electricity in the anomalous current in a dielectric as belonging to one of the following three types: (1) translation of free electrons as in metallic conduction; (2) transfer of charges and movement of ions as in electrolysis; (3) separation of charges within the molecule so that its electric moment increases.

Now Thornton [36] has found that the period of oscillation of a flint glass ellipsoid polarized to constancy in a stationary field remains unchanged when the ellipsoid is exposed to radiation from radium bromide. If the charge had been free it would have been removed and the period would have changed. The polarization of the glass then seems to be of class (3) above.

If we may assume that vitreous silica, and also quartz in the direction perpendicular to the axis, would behave similarly to flint glass, then the process of dielectric polarization in these cases, according to Thornton, might consist of: first, the production of charged isolated units (molecules); second, a further separation of the charges because of the attraction and quasi-elastic approach of opposite charges on adjacent molecules; third, the gradual establishment of electric strain throughout the material, under new conditions of internal stress set up by the first polarization.

In the case of quartz in the axial direction, on the other hand, there has been so much evidence of electrolytic conduction already cited that we may well believe it possible that Thornton's experiment would have shown a dissipation of the free charge. For the explanation of the anomalous currents in the axial direction it is reasonable to look first to the peculiarities of the transport of electricity in an ionized medium.

Taking quartz as a whole, with anomalous dielectric displacements in one direction and anomalous conductivities in another, we may expect the quantitative explanation of its dielectric properties to be a rather

[36] Article cited in note [2].

complex affair. It seems to me that not much is to be gained by further experiments on natural quartz until the true axial conductivity of pure quartz shall have been elucidated.

Effect of micro-twinning

Ferry observed that the difference between the dielectric constant at high and at low frequencies was accentuated in crystals which showed Airy spirals in polarized light, although it was not possible to obtain very accurate values for the constant. Such crystals contain thin laminae in twinned relationship. The result stated is thus in agreement with Maxwell's theory of the effect of a laminated structure on the dielectric properties, but in this instance the lamination is real and not hypothetical.

Other forms of silica

The only test of the conductivity of tridymite on record is one by Beijerinck, who classes it with quartz as a non-conductor. As his limit of sensitivity was only ¼ megohm per sq. cm per cm, this does not tell us very much.

Cristobalite has not been examined, but the fact may be noted here that the conductivity of vitreous silica at 1260° increases with the progress of its devitrification to form cristobalite.[37]

[37] Pirani & Siemens, article cited in note [32].

Chapter XXVIII. PIEZO-ELECTRIC AND PYRO-ELECTRIC PROPERTIES

Piezo-electricity

The interconversion of mechanical and electrical energy (see Table II) is exemplified by the behavior of crystals of certain substances, which when stressed by non-uniform pressure or by torsion, develop electric charges on parts of their surfaces. Conversely, when such a crystal is placed in an electric field, it becomes distorted thereby.

The term *piezo-electricity* is properly used to include not only the separation of electric charges as the result of mechanical stress, producing an electric field; but also the reverse effect of the production of mechanical strain by an applied electric field. A narrower usage would confine "piezo-electricity" to the first effect alone, while the reverse effect would be classed as one of the types of *electro-striction*.

A large amount of experimental and theoretical work has centered about the piezo-electric properties of quartz. The piezo-electric properties of the other forms of silica have not been investigated.

Quantitative statement of the phenomena

When a crystal of quartz of the usual shape is compressed in the direction of an equatorial (twofold) symmetry-axis, the six edges of the prism become electrically charged, the charges being alternately positive and negative when observed in serial order around the equatorial circumference of the crystal. Other directions of compression yield more complex distributions of charges, and the compression, extension or bending of plates of various shapes and orientations give results which were found by the early experimenters to be very difficult to analyze, even qualitatively. It is easy to see, then, that the complete quantitative statement of the piezo-electric effects in a fragment of crystal of any random shape is somewhat involved.

The charge per unit area, at a constant temperature, is found to be directly proportional to the force of compression or tension, and independent of the thickness of material acted upon. This fact may be combined with Hooke's Law of the proportionality of stress and strain, in the statement that the electric field intensity is proportional to the strain. This linear relationship furnishes the basis for a complete mathematical description of the phenomena of piezo-electricity.

To take the most general case: any stress will produce a strain, as defined and described in XXIII. This strain is resolvable into 6 components. The electric field requires for its complete description 3 components. Thus there will be required $3 \times 6 = 18$ equations, with 18 constants, for

the complete statement of the electric effect of any stress on any fragment of a crystalline substance.[1]

These 18 parameters may take the form of ratios between the electric moments per unit of volume and the displacements, and are then called *piezo-electric moduli*.[2] Or they may be put in the form of ratios between electric moments and pressures, and are then called *piezo-electric coefficients*.[2]

In any but the most general case the number of constants is reduced by the symmetry of the substance. The symmetry of low-quartz, and

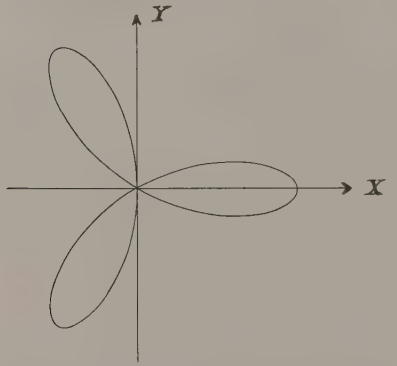


FIG. XXVIII.1.

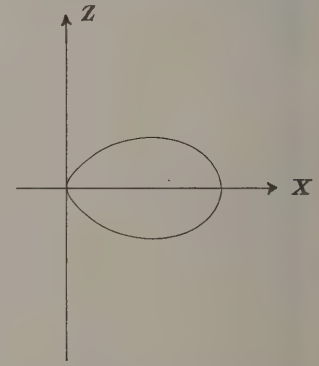


FIG. XXVIII.2.

FIG. XXVIII.1.—Equatorial (horizontal) section of the surface which represents the longitudinal excitation of electric charges in quartz due to a linear force of compression or tension.

FIG. XXVIII.2.—Axial (vertical) section of the surface which represents the longitudinal excitation of electric charges in quartz due to a linear force of compression or tension.

the simplifications of the equations caused by making two of the coordinate axes coincide with axes of symmetry (see Fig. XXIII.8), lead to a reduction in the number of constants needed for low-quartz from 18 to 2.

PHENOMENA IN LOW-QUARTZ

Equations can be derived, containing 2 piezo-electric constants or 2 piezo-electric moduli, which give a complete statement of the electric effects of any system of stresses on a plate of quartz. The case of most practical interest is that of a linear compression or tension on a plate

[1] See VOIGT, W., *Lehrbuch der Kristallphysik* (1910, Leipzig) pp. 801-937. RIECKE, E., *Pyroelektrizität und Piezoelektrizität* in Graetz's *Handbuch der Elektrizität*, etc. (1918, Leipzig) Vol. I, pp. 342-420.

[2] As in the case of the elastic coefficients and moduli (see XXIII, note [1]) Voigt's use of the terms is just the opposite of that established by previous custom and followed in this book. Riecke follows Voigt's usage.

oriented in some definite way with respect to the principal axis of the quartz. The excitation of charges in the direction of the pressure may be represented by plotting the constant of proportionality between pressure and dielectric moment as a radius vector measured in the direction of the pressure. This yields a surface of 3 similar sheets [3] whose equatorial section is shown in Figure XXVIII.1, while the vertical section of any one of the three sheets is shown in Figure XXVIII.2.

The three equatorial (twofold horizontal) symmetry axes of low-quartz, along which the effect is a maximum, are sometimes called *electric axes*. Compression in the direction of such an axis produces positive and

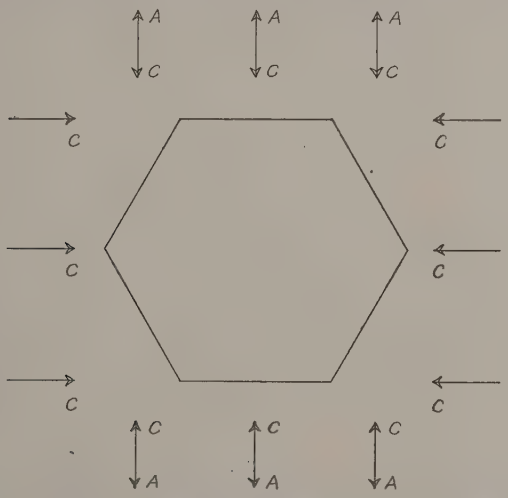


FIG. XXVIII.3.—Diagram to illustrate the relation of strain to sign of charge in low-quartz. (Kelvin.)

negative charges on the opposite faces of a rectangular parallelepiped having a pair of faces cut ⊥ to that particular axis. Tension produces charges of the opposite sign. These phenomena are often referred to as the "direct longitudinal effect". On the other hand, compression *perpendicular* to this axis, in the horizontal plane, again produces positive and negative charges on those same faces, but opposite in sign to the charges produced by compression *along* the axis; and tension, in turn, reverses this effect. These phenomena are referred to as the "direct transverse effect."

Thus compression in the one direction produces the same effect as tension in the direction ⊥ thereto.

This relation follows very simply from the geometry of the crystal,

[3] See VOIGT, W., book cited, pp. 848-864.

as was pointed out by Kelvin.[4] Imagine an elongation A to be produced in the horizontal plane of a crystal, as shown in Figure XXVIII.3. Superpose on this two equal but negative elongations, represented by C, one in the direction of the original elongation and the other ⊥ thereto. These negative elongations are equivalent to a uniform condensation, which is without electrical effect, and they therefore leave the original electrical effect unchanged. But the only remaining elongation is now a negative one ⊥ to the original positive elongation, and the electric effects of these last-mentioned two are thus seen to be equal. This special case is of course included in Voigt's general equations.

Since rotating the compression, so to speak, by 90° causes a change of sign from positive to negative, it seems reasonable to expect that for some intermediate direction of compression the effect would be zero, but, as Kelvin showed, such zero axes do not exist in the horizontal plane. Any elongation whatever in the horizontal plane produces an electric effect. Zero effect can be produced only by two equal simple elongations which are either coincident and opposite, or ⊥ and alike.

It remains true, nevertheless, that the excitation of charges on surfaces normal to the direction of pressure does pass through zero 6 times in the course of one complete rotation about the axis. These directions were called by Röntgen[5] "Axen fehlender Piezoelektricität."

These relations are evident from the more general considerations of Voigt, as expressed in Figure XXVIII.1.

It is also evident from Figures XXVIII.1 and XXVIII.2 that compression or tension in the direction of the principal axis of quartz produces no electrification. A small degree of electrification has been reported by some investigators, but this was probably due either to stress at a slight angle to the axis, or to some imperfection in the crystal.

Uniform (hydrostatic) pressure should produce no piezo-electric effect in quartz. This expectation has been confirmed by Koch,[6] who compressed a disk (6×18 mm) and a parallelepiped ($20 \times 10 \times 10$ mm) under mineral oil to a pressure of about 300 megabaryes, the silvered surfaces being connected to a Hankel electrometer with sensitivity of 1 millivolt. Both specimens gave deflections which persisted only about 20 seconds and were evidently due to non-uniform heating of the specimens by the oil, which is slightly warmed by the compression. The effects are similar to those produced by warming the specimens in a current of warm air.

Piezo-electric phenomena are produced not only by tension and compression, but also by torsion. The phenomena have been carefully studied

[4] Kelvin, *On the piezo-electric property of quartz*, Phil. Mag. (1893) **36**: 331-340.

[5] Röntgen, W. C., *Ueber die durch electrische Kräfte erzeugte Aenderung der Doppelbrechung des Quarzes*, Ber. Oberhess. Ges. Natur-u. Heilkunde (1883), **22**: 49-64, 98-116; Ann. Phys. u. Chem. (Wiedemann), (1883), **18**: 213-228, 534-551. Kelvin (article cited, p. 339) was wrong in ascribing to Röntgen the opinion that there are directions of compression which produce no electric effect whatever.

[6] Koch, P. P., Ann. Physik (1906) (4) **19**: 567-586.

by Voigt & Fréedericksz [7] and found to be in complete agreement with the general principles already set forth.

The torsion of a cylinder whose axis is parallel to the principal axis of the quartz itself produces no piezo-electric effect. Cylinders oriented in other directions give effects calculable from the two constants of quartz.

Bending also produces piezo-electric phenomena, shown by Voigt & Fréedericksz to be in accord with the general principles and calculable from the two constants. Bending due to the action of a moment about a line transverse to the cross-section of a cylinder of quartz is without electrical effect if the axis of the cylinder is $\parallel$ either to the principal axis or to one of the equatorial symmetry axes of the quartz. Charges are produced if the cylinder is $\parallel$ to a so-called "intermediate axis" ($\perp$ to principal axis and one equatorial axis, see p. 188).

Numerical data on quartz

The most probable values of the two piezo-electric coefficients of quartz at room temperature are:

$$d_{11} = -69 \times 10^{-9}$$
$$d_{14} = 17 \times 10^{-9}$$

pressures being stated in baryes (dynes per sq. cm) and electric charge in absolute electrostatic units (e. s. u.) per sq. cm.

The coefficient d_{11} is the one concerned in the electrification of plates of quartz by forces in the equatorial plane and $\parallel$ or $\perp$ to the electric axes, and is the one which was measured in the earlier experiments on piezo-electricity of quartz. It is the proportionality factor between charge per unit area and pressure.

The coefficient d_{11} is constant within 0.1 per cent up to a pressure of at least 3450 megabaryes.

It is also relatively independent of temperature down to liquid hydrogen temperatures or up to about 200° C, but the change then begins to be easily appreciable. The coefficient falls more and more rapidly at higher temperatures until at the inversion point (573°) it becomes zero.

The effects of pressure and temperature on the coefficient d_{14} are not known.

Constancy of the coefficient d_{11}

There is a troublesome discrepancy in the experimental determinations of the piezo-electric coefficient d_{11}. The determinations accepted in this book as a basis for the value 69×10^{-9} are the following:

J. Curie	-69.0×10^{-9}
Röntgen & Joffé	-69.4×10^{-9}

[7] Voigt, W., & Fréedericksz, V., *Theoretisches und Experimentelles zu der piezoelektrischen Erregung eines Kreiszylinders durch Drillung und Biegung,* Ann. Physik (1915) (4) **48**: 145-176.

but there is a series of other determinations which appear in many respects equally dependable, yet give a mean value of only about 63×10^{-9}, 9 per cent lower than those first cited. The low determinations are:

		$-d_{11} \times 10^9$
J. Curie & P. Curie	1881	63.
Czermak	1887	63.
Riecke & Voigt	1892	64.5
Pockels	1894	62.7
Hayashi	1912	63.1
		63.3

It is difficult to see why all of these should be so much lower than the values obtained by J. Curie and by Röntgen & Joffé, particularly in view of the fairly good agreement among them. There is this to be said, however, that practically all of the causes of error tend toward *low* values. This is true of errors in the orientation of the plate, of underestimation of the capacity of the condenser, of twinning or intergrowths in the crystal, of the presence of initial stresses, and of failures of insulation, and probably also of inhomogeneity in the distribution of tension.

It may also be that there are considerable differences between the values of the coefficient for different specimens of quartz. This possibility has not been investigated.

The character of the stress may be of importance. It is significant that the two high values (J. Curie and Röntgen) were obtained with plates in tension, while most of the low values (Czermak, Riecke & Voigt, Pockels, Hayashi) were obtained by compression. No very precise comparison of these two methods of stressing the specimen has been made.

Experimental data on the coefficients

The "piezo-quartz" plate used by the Curies and by other experimenters is a plate cut $\perp$ to an electric axis (axis of twofold symmetry) and with its long dimension $\perp$ to the principal (threefold) axis of the quartz (see Fig. XXVIII.4). Its shape is thus like a wooden joist or plank. Tension is applied in the direction of the long dimension of the plank. The two flat sides are covered with a conducting coating and the charges which appear on these surfaces are measured or used for other purposes.

Disregarding $+$ and $-$ signs, the charge, q, per unit area is proportional to the pressure, P: $q = d_{11} P$. If the plate is l_1 cm long, l_2 wide, and l_3 thick, the total charge Q on one of the coated surfaces is $Q = l_1 l_2 q$, and the total load W supported by the plate is $W = l_2 l_3 P$. It follows, therefore, that $Q = d_{11} \frac{l_1}{l_3} W$. In other words, the total charge on the flat face of such a plate, with a given load, is proportional to its length and inversely proportional to its thickness, but independent of its width.

The most reliable determinations of the principal piezo-electric coefficient d_{11} have been made on plates of the above-described character by J. Curie and by Röntgen & Joffé.

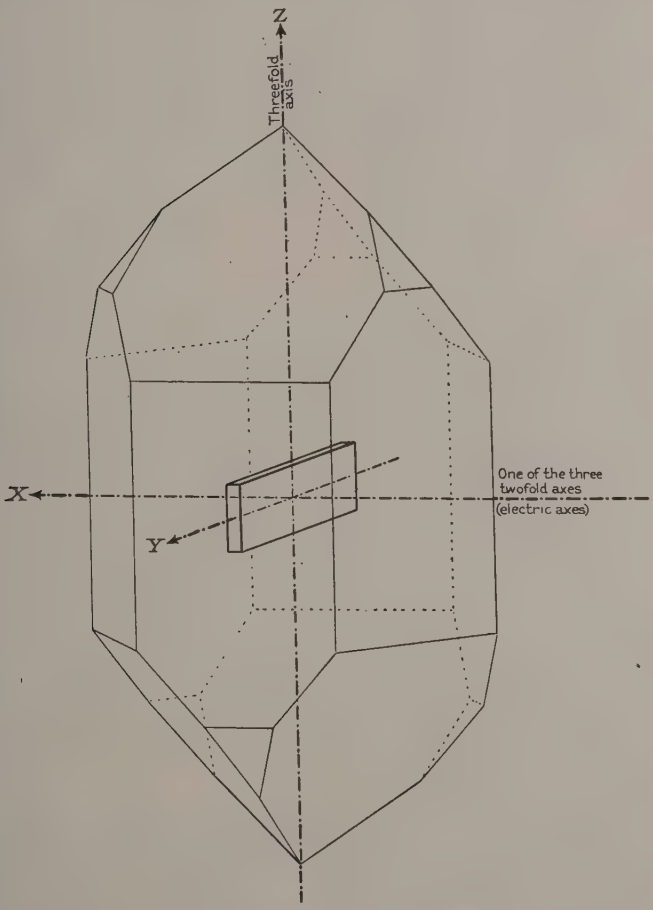


FIG. XXVIII.4.—Usual orientation of a "piezo-quartz plate" in a crystal of quartz.

Curie.—Determinations of the principal piezo-electric coefficient d_{11} were made by J. Curie[8] before 1910. The determination is in terms of a battery of 10 Weston cells as standard. These cells serve to charge a condenser about

[8] Quoted by CURIE, Mme. P., *Traité de radioactivité* (1910, Paris) Vol. 1, pp. 95-106.

20 cm in diameter, of measured dimensions. This known charge can be matched, with the aid of a sensitive electrometer, by an equal charge obtained by adjusting a weight acting upon the quartz plate which is being tested. 12 plates tested by this method gave the mean value 0.0677 with the weight given in kg, corresponding to 69.0×10^{-9} in terms of the tension in baryes.

Röntgen & Joffé.—The determinations by Röntgen & Joffé[9] were made by a similar method, with 4 to 6 cadmium normal cells as standard and an air condenser of about 21 cm diameter whose inter-plate distance was varied from about 2 to 5 mm. A small correction was made for lack of planeness in the condenser plates revealed by this variation. Three quartz plates about $70 \times 20 \times 0.6$ mm, with silvered surfaces, yielded the following values of d_{11}:

No. I	69.5×10^{-9}
No. II	69.5×10^{-9}
No. III	69.2×10^{-9}
Mean	69.4×10^{-9}

These plates were obtained at different times, but from the same manufacturer (in Paris) and are presumably from the same stock material. They were shown optically to be free from intergrowths.

A fourth plate, larger than the other three, and made by another manufacturer, gave a charge 0.8 per cent lower, but was found to have been oriented in cutting 1 or 2 degrees off from perpendicularity to an electric axis. Deviations of 1, 2, or 3 degrees can be shown by calculation to produce deviations in the charge amounting to 0.14, 0.55, and 1.33 per cent, respectively. The difference is therefore accounted for.

The same three plates, when covered with tin-foil, gave results about 1 per cent lower, because part of the stress was taken up by the tin-foil and its adhesive.

Other determinations of d_{11}

There are 5 other sets of determinations of d_{11}, all of which are considerably lower than the value which I have adopted as most probable. These have already been listed and will now be briefly reviewed.

J. & P. Curie.—The phenomenon called "piezo-electricity" was discovered by the brothers Jacques and Pierre Curie[10] in 1880, and they made the first determination of the constant.[11]

The Curies made their early measurements on a parallelepiped of quartz with one pair of faces $\perp$ to the principal axis, and a second pair $\perp$ to an equatorial (twofold) axis, the third pair being accordingly $\parallel$ to both axes. Pressure was applied either to the second or the third pair of faces. Details of the measurement are not given, but it was found that a weight of 1 kg on the plate disengaged a quantity of electricity sufficient to charge a sphere 16.6

[9] Röntgen, W. C., & Joffé, A., *Über die Elektrizitätsleitung in einigen Kristallen und über den Einfluss der Bestrahlung darauf, I.*, Ann. Physik (1913) (4) **41**: 449-498.

[10] Curie, J., & Curie, P., *Développement, par pression, de l'électricité polaire dans les cristaux hémièdres à faces inclinées*, Compt. rend. Acad. Paris, (1880), **91**: 294-295; Bull. Soc. Mineral. France, (1880), **3**: 90-93.

[11] Curie, J., & Curie, P., Compt. rend. Acad. Paris, (1881) **93**: 204-207.

cm in diameter to the potential of a Daniell cell, or a quantity of 0.062 e. s. u., equivalent to the value $d_{11} = 63 \times 10^{-9}$ when the pressure is in baryes.

Czermak.—Czermak's[12] measurements were made on two prisms of quartz cut from two cylinders on which a series of qualitative tests had previously been made, about 20 mm long by 15 mm diameter with axes $\parallel$ to the axis of the quartz. A pair of faces of one of the prisms were cut $\perp$ to an electric axis, while those of the other prism were turned about 12 degrees off perpendicularity. The charges on the compressed faces were measured by means of a Hankel electrometer in connection with the known capacity of the metal parts. This capacity datum is the weak point of the determination, since it rests upon two measurements of capacity which differed by 6 per cent. The final value is 0.061 e. s. u. per kg, or 63×10^{-9} for d_{11}.

Riecke & Voigt.—Riecke & Voigt[13] used four plates of quartz cut from a single plate about 6 mm thick $\perp$ to an electric axis. The longer edges of the small plates were at angles of 22½ or 45 degrees to the principal axis of the quartz. Pressures were applied both $\perp$ and $\parallel$ to the selected electric axis, and charges were measured on the surfaces $\perp$ to that axis. A Clark cell served as standard of e. m. f. The results of 5 series of measurements were reduced by least-square adjustment to an equation for the piezo-electric moment in terms of the two piezo-electric coefficients in arbitrary units. These were converted to absolute measure through determining the capacity of the condenser and electrometer used in the series by means of Maxwell's tuning-fork method, yielding the following results:[14]

$$d_{11} = \quad 64.5 \times 10^{-9}$$
$$d_{14} = -\ 14.5 \times 10^{-9}$$

Pockels.—The measurements of Pockels[15] were very similar to those of Riecke & Voigt, except that pressures were applied only in directions $\perp$ to an electric axis, while charges were measured on faces $\parallel$ to the direction of pressure transverse effect). 5 series were made on 3 plates with faces $\perp$ to an electric axis and long edges at 90, $+45$, and -45 degrees, respectively, to the principal axis. All were cut from untwinned parts of the same crystal of left-quartz, supposed to be from Brazil. The capacity of the accompanying air condenser was calculated from its dimensions. The results are:

$$d_{11} = -\ 62.7 \times 10^{-9}$$
$$d_{14} = \quad 19.25 \times 10^{-9}$$

Hayashi[16] measured the constant incidentally to a series of measurements on the pyro-electricity of various substances, for which he used a quartz plate

[12] Czermak, P., *Über das elektrische Verhalten des Quarzes,* Sitzungsb. Kais. Akad. Wiss. Wien, Math. Nat. Cl. (1887) **96, II**: 1217-1244.

[13] Riecke, E., & Voigt, W., *Die piezoelectrischen Constanten des Quarzes und Turmalines,* Ann. Phys. u. Chem. (Wiedemann) (1892) **45**: 523-552.

[14] The signs are opposite to those given at p. 559, since the positive direction of the X-axis was taken opposite to that now generally adopted and shown in Figure XXVIII.4.

[15] Pockels, F., *Ueber den Einfluss des elektrostatischen Feldes auf das optische Verhalten piëzoelektrischer Krystalle,* Abhandl. Kön. Ges. Wiss. Göttingen (1893), **39**, 206 pp.

[16] Hayashi, F., *Beobachtungen über Pyroelektrizität,* Inaug.-Diss., Göttingen, 1912, 49 pp.

as a compensating source. To determine the constant he employed an octagonal prism about 20 mm high, compressed by means of a lever with traveling weight, and took off the charge from one of the compressed surfaces to an air condenser and Hankel electrometer. This charge was made to compensate the charge delivered by a Harms condenser, with calibrated millivoltmeter. The Harms condenser was calibrated in terms of a standard capacity and also by comparison with a variable air condenser, the two methods agreeing within 0.2 per cent. Two series of 41 settings each on each of two quartz prisms gave mean ratios of load to charge agreeing within 0.1 per cent and yielding the value 63.1×10^{-9} for d_{11}.

The coefficient d_{14}

Only two determinations have been made of the second piezo-electric coefficient, d_{14}, which comes into play when the stress is not in the equatorial plane. These determinations have been made by Riecke & Voigt and by Pockels, in researches already referred to. Their results are:

Riecke & Voigt	14.5×10^{-9}
Pockels	19.25×10^{-9}

The value 17×10^{-9} has therefore been adopted as the most probable but the question of the constancy of d_{14} deserves further examination (see p. 559).

Effect of pressure on the coefficient d_{11}

Nachtikal[17] examined the question of the change of the coefficient d_{11} with pressure. The apparatus made was similar to that of Riecke & Voigt.[18] A plate was loaded with different initial pressures in the direction of an electric axis and the effect of an additional increment of pressure was then tested. The results indicate a decrease in the numerical value of the coefficient with increasing pressure, over the range 6 to 22 megabaryes, expressed by the formula

$$-d_{11} = 65.4 \times 10^{-9} - 0.105 \times 10^{-15}\ p$$

when p is given in baryes. The changes observed (about 0.16 per cent per megabarye) were not, however, appreciably larger than the possible experimental error.

Röntgen[19] examined into the matter further in 1913, and could find no change in the coefficient greater than 0.4 per cent for tensions ranging from 0.3 to 18 megabaryes.

Karcher[20] has subsequently found that the relation of charge to pressure

[17] Nachtikal, F., *Ueber die Proportionalität zwischen den piezoelectrischen Momenten und den sie hervorrufenden Drucken,* Nachr. Kön. Ges. Wiss. Göttingen, Math. phys. Kl. 1899: 109-118.

[18] Article cited.

[19] Röntgen, W. C., & Joffé, A., article cited.

[20] Karcher, J. C., *A piezo-electric method for the instantaneous measurement of high pressures,* Sci. Pap. Bur. Standards, (1922), **18**: 257-264, (No. 445).

is linear up to 3450 megabaryes. The relation was tested with a precision of 0.1 per cent by observing the throw of a ballistic galvanometer when the pressure on a quartz plate in a testing-machine was suddenly released.

Experimental evidence obtained by Karcher at the U. S. Bureau of Standards (not published) indicates that the proportionality of pressure and charge holds for all rates of application of the pressure which are experimentally obtainable, namely, rates up to those of the order of 1 megabarye change of pressure per 0.000 01 second.

EFFECT OF TEMPERATURE ON THE COEFFICIENT d_{11}

The change of d_{11} at low temperatures has been examined by Lissauer, by Röntgen, and by Kamerlingh Onnes & Beckman; and at high temperatures by Perrier.

Lissauer [21] found that d_{11} does not change by more than 2 per cent when the temperature is lowered from 19° to —192°C.

Röntgen's tests [22] confirm this statement. He found that the change from room temperature to that of liquid air has so little effect on the piezo-electric coefficient of quartz that its variation between 15 and 25°C may be considered to be within the limits of precision of its measurement.

The most exact test of the change at low temperatures is by Kamerlingh Onnes & Beckman.[23] Two quartz plates about 70 to 80 mm long, 20 mm wide, and 0.6 mm thick, were arranged to be stressed by tension. One of the coated surfaces of each plate was earthed, while the other two were both connected to a pair of quadrants of an electrometer. Plate 1 remained at room temperature, while plate 2 could be cooled in a Dewar tube. The charges developed by loading each plate separately were read in terms of the electrometer deflection. The readings are therefore relative, since the capacity under each set of conditions is not known exactly. The results are:

Temperature ° K	Change from room temperature, per cent		
	Plate 1	Plate 2	Difference (2)—(1)
78.5	+ 2.4	+ 1.1	— 1.3
20.3	+ 2.2	+ 1.0	— 1.2
80.0 *	+ 2.1	+ 0.9	— 1.2

* Rubber diaphragm on Dewar tube omitted.

The coefficient d_{11} evidently decreases about 1.2 per cent when quartz is cooled from room temperature to that of liquid air, and changes by less than 0.2 per cent on further cooling to the temperature of liquid hydrogen.

[21] Lissauer, W., Dissert., München, 1907, quoted by Voigt, W., book cited, p. 862.
[22] Röntgen & Joffé, article cited (1913).
[23] Onnes, H. Kamerlingh, & Beckman, Mrs. A., *On piezo-electric and pyro-electric properties of quartz at low temperatures, down to that of liquid hydrogen*, Proc. Acad. Sci. Amsterdam, (1913) **15**: 1380-1383; Comm. Phys. Lab. Leiden, No. 132 f; Versl. Kon. Akad. Wet. Amsterdam, (1913) **21**: 1277-1281.

High temperatures

According to Perrier,[24] the piezo-electricity of quartz is independent of temperature at temperatures not far above that of the room. Beginning at about 200°, the piezo-electricity decreases with rising temperature, until at 579° it disappears suddenly and completely. On cooling it reappears at 576°, thus showing the temperature hysteresis characteristic of other properties at the inversion (see VII).

As we have seen, the piezo-electric coefficient is practically independent of temperature at room temperatures. Young's modulus of elasticity perpendicular to the axis is also nearly independent of temperature under these conditions. It follows therefore that the electric moment produced by a given deformation of quartz depends almost entirely on the deformation itself, without regard to the temperature.

The piezo-electric moduli of quartz

The piezo-electric moduli (termed "piezo-electric constants" by Voigt and by Riecke) express the electric moments in terms of displacements instead of pressures, and are related to the piezo-electric coefficients by the formulas:

$$e_{11} = d_{11}(c_{11} - c_{12}) + d_{14}c_{14}$$
$$e_{14} = 2d_{11}c_{14} + d_{14}c_{44}$$

where c_{11}, c_{12}, c_{14}, c_{44} are elastic moduli (see p. 434). Voigt's values for these moduli (Tab. XXIII.16), combined with the values of d_{11} and d_{14} adopted in this chapter, yield the following values for the piezo-electric moduli, pressure being in baryes (dynes per sq. cm):

$$e_{11} = -51.0 \times 10^8$$
$$e_{14} = -13.5 \times 10^8$$

The converse piezo-electric effect

The electric field of a charged piezo-electric plate represents stored energy, which must have come from a displacement of the constituent particles of the quartz under the applied force. Lippmann [25] therefore predicted that the act of charging a quartz plate from an external source of electricity would be found to cause a deformation of the same general character as that which would have been caused by a stress of the magnitude necessary to develop the charge piezo-electrically. This prediction was soon confirmed by the Curies,[26] who showed that the deformation is of the order of magnitude predicted.

[24] Perrier, A., Arch. sci. phys. nat. (1916) (4) **41**: 492-497.
[25] Lippmann, G., Ann. Chim. et Phys. (1881) (5) **24**: pp. 164-167.
[26] Curie, J., & Curie, P., *Déformations électriques du quartz,* Compt. rend. Acad. Paris (1882) **95**: 914-917.

In plates cut ⊥ to an electric axis we may therefore speak of the "converse longitudinal effect" or the "converse transverse effect," according to whether we are considering deformation ∥ or ⊥, respectively, to this electric axis. (See p. 557.)

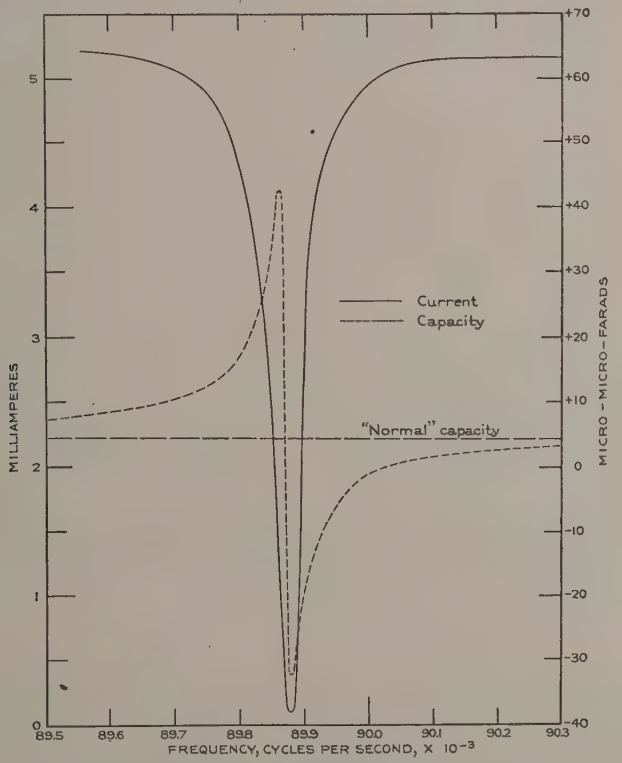


FIG. XXVIII.5.—Electric effects of a quartz plate in a circuit carrying a current having a periodicity near that of the mechanical vibration of the quartz. Cady, 1922.

An interesting case of the interconversion of electric and mechanical energy is afforded by the vibrations of a plate or bar of quartz. A bar of quartz cut like a piezo-electric plate (see Fig. XXVIII.4) placed between, but not in contact with, two metallic electrodes which are in the grid circuit of a radio oscillating tube, is subjected by the periodic variation of the voltage in the circuit to a periodic mechanical stress. If the frequency of this periodic stress is very near the natural frequency of longitudinal vibration of the bar, or one of its harmonics, the bar will be set into vigorous mechanical vibration. This vibration, in turn, pro-

duces a periodic variation of piezo-electric potential difference which reacts on the electric circuit. In other words, the bar can be made to act as a resonator for the circuit.[27]

The natural damping of the vibration in quartz is so small that the bar responds only to a narrow range of frequencies. Through its reciprocal electric action on the circuit it therefore accurately controls the frequency of the circuit, which need not be tuned at all closely for resonance at this frequency. Small variations due to miscellaneous electrical causes are thus rendered practically without effect in such a circuit.

So far as its reversible action is concerned, the quartz plate is equivalent to a capacity which rises rapidly with the frequency as the critical resonance frequency is approached, then falls and becomes negative,—that is, equivalent to an inductance,—at frequencies just above the critical value. This is illustrated by Figure XXVIII.5.

High-quartz

The symmetry of high-quartz is hexagonal trapezohedral (enantiomorphous hemihedral). The piezo-electric constants reduce in this case to one coefficient, d_{14}, when two coordinate axes coincide with axes of symmetry (see pp. 189, 556). Piezo-electric phenomena due to linear stresses should therefore disappear at the inversion-point, 573°. This has been found to be true by Perrier.

On the other hand, piezo-electricity due to torsion should persist. This has not been tested experimentally. The form of the curve of d_{14} against temperature, through the inversion-point, would contribute additional evidence to what we already have on the atomic and structural changes at that point.

Theory of piezo-electricity in quartz

The most important early contribution to the theory of piezo-electricity of quartz was made by Kelvin[28] in 1893. Recognizing that electric aeolotropy of a "molecule,"—better called simply an "atom-group" in the solid state,—and nothing but electric aeolotropy of the molecule, can account for piezo-electricity, Kelvin assumed the existence of a unit of structure containing 3 Si and 6 O, equivalent to 3 SiO_2. As the simplest possible mode of arrangement, the 9 atoms are assumed to be arranged in a circle in a plane $\perp$ to the principal axis of the quartz crystal, the circular groups, in turn, having an hexagonal pattern. The structure is illustrated in Figure XXVIII.6. The + sign indicates a silicon atom, the — sign a *pair* of oxygen atoms (or vice versa, so far as the electrical theory is concerned).

[27] Cady, W. G., *The piezo-electric resonator,* Proc. Inst. Radio Engineers (1922) **10**: 83-114.

[28] Kelvin, article cited in note [4]. Also, *On the theory of piezo-electricity of crystals,* Phil. Mag. (1893) (5) **36**: 453-459.

An attraction may be supposed to exist between a + unit of one circle and the nearest — unit of a neighboring circle. This force fixes the orientation of the circles in their plane, and also makes necessary a relative displacement of the + and — units if the crystal as a whole is distorted by an outside force.

Suppose now that pressures and tensions are applied to the crystal such that a simple elongation is produced in a direction ⊥ to the horizontal

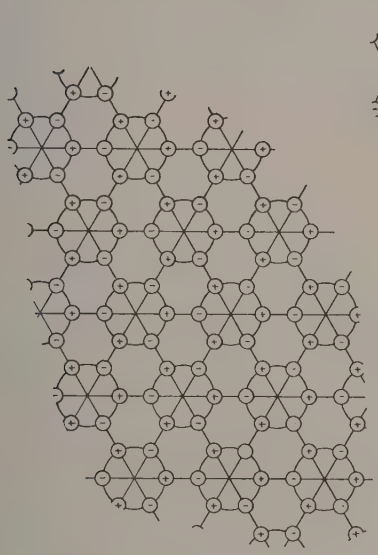


Fig XXVIII.6.

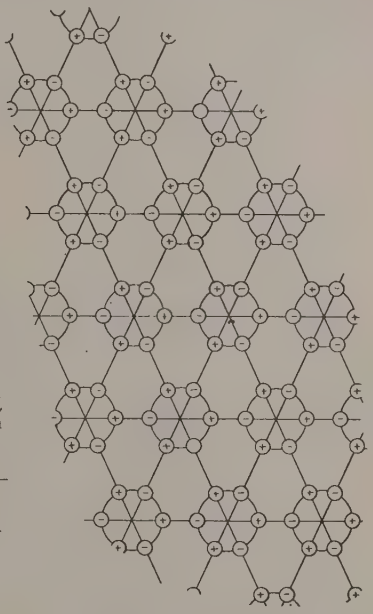


Fig. XXVIII.7.

Fig. XXVIII.6.—Pattern assumed by Kelvin to aid in explaining the piezo-electricity of low-quartz.

Fig. XXVIII.7.—Effect of elongation of the pattern of Figure XXVIII.6 by external forces.

rows of circles in Figure XXVIII.6, and let it be assumed that there is freedom of movement and that the forces between the + and — units of neighboring circles keep them always alined in straight lines through the centers of the circles. Then the distorted pattern will be as represented in Figure XXVIII.7. Two of the three diametral lines in each circle are altered in direction, while the third remains unchanged. The distances apart of + and — units along the horizontal diameters in the figure remain unchanged, while in lines ‖ to and on either side of these diameters are found + and — units which have been brought nearer together than before.

The electric effect, at a distance, of this displacement of charges, expressed as the electric moment m per unit volume, is

$$m = Nq.4r\Phi \cos 30° = 2\sqrt{3}\, Nrq\Phi$$

in which N = number of "circles" per unit volume,
q = quantity of electricity on each + or — unit,
r = radius of the circle,
Φ = angular displacement of one of the displaced diameters.

To test the magnitude of the effect Kelvin assumed the following numerical data (a = radius of + or — unit):

$N = 10^{21}$ per cc
$r = \frac{1}{4}\, N^{-1/3} = 0.25$ mμ
$a = 0.2\, r$
$q = 0.002\, a$

Then $m = 866\, \Phi$. From Curie's measurements $m = 0.063$ e.s.u. per cc for a force of 1 kg per sq. cm, whence $\Phi = 0.000\ 73$ radian, which is a displacement of reasonable magnitude for such a force.

Kelvin [29] stated his theory of piezo-electricity clearly in his favorite way, namely, with the aid of a workable experimental model, of a type which had been suggested by the Curies [30] years before but had been overlooked and forgotten. Kelvin first describes the construction of a piezo-electric pile, consisting of a pile of double plates, each made of zinc and copper soldered together face to face; these plates are held apart, with a few mm air space, by means of soft rubber separators. Each plate is the analog of an elementary "molecule" with a difference of potential between its two sides. If a weight is placed on the top of the pile, the "molecules" are brought a little closer together by the compression of the rubber and a positive charge is squeezed out, so to speak, on to the upper surface of the topmost plate; its presence there can be shown with an electrometer.

The model can be generalized by taking as the crystalline molecule a rigid body bounded by a surface made up of pieces of different metals, soldered together to make a continuous conducting surface. A number of such molecules are arranged in space according to some space-lattice and are held together by non-conducting springs connecting each one with those of its neighbors which are relatively near. This makes a complete model for elasticity and piezo-electricity.

The same model will serve also for pyro-electricity if it be supposed that a change of temperature produces either a change of the contact potential difference of the metals or a change of configuration of the assemblage of molecules; the change of configuration being caused either

[29] Kelvin, *On a piezo-electric pile*, Phil. Mag. (1893) **36**: 342-343, 384.
[30] Curie, J., & Curie, P., Compt. rend. Acad. Paris (1881) **92**: 350-353.

by a change in shape of the molecules or a change in the force of the springs.

The theory has been developed in more general form by Riecke,[31] assuming five different simple "pole-systems" to accord with the various symmetries to be considered.

The requirements for low-quartz are met by the combination of a trigonal pole-system in "position I" and a dihexagonal pole-system. These are illustrated in Figures XXVIII.8 and XXVIII.9. In each case the assumed molecule has a singular axis. The trigonal system has 6 poles arranged at the corners of a hexagon in a plane $\perp$ to the axis, with coordinates placed as shown in Figure XXVIII.8. The length of the side of the hexagon is α. (Position II differs from position I only in having the axis η instead of ξ pass through a positive pole.)

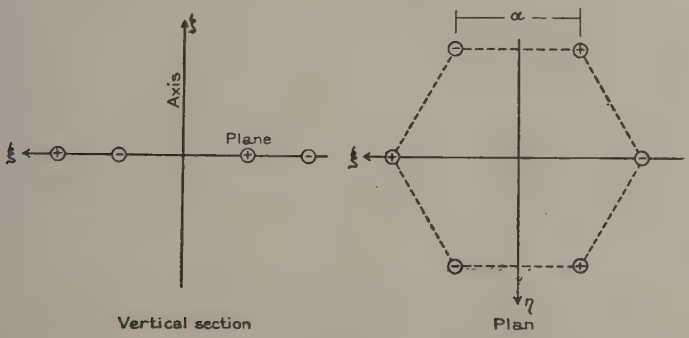


FIG. XXVIII.8.—Trigonal pole-system, position I.

The dihexagonal system has two sets of 12 poles each, in two $\parallel$ planes $\perp$ to the axis. The distance of a given pole in the upper plane from the center of the assumed molecule is δ, and the angle which the direction of δ makes with the axis ζ is θ.

The potential of the trigonal system at a distance is

$$E = 6a_3{}^3\varepsilon\alpha^3$$

and that of the dihexagonal system is

$$H = 48\, a_6{}^7\varepsilon\delta^7 \cos\theta\sin^6\theta$$

in which ε is the charge on each pole and a_3 and a_6 are constants which follow from the theory of spherical functions.

The assumed molecules are supposed to be arranged according to a space lattice having trigonal trapezohedral symmetry.

[31] RIECKE, E., *Molekulartheorie der piezoelektrischen und pyroelektrischen Erscheinungen,* Abh. K. Ges. Wiss. Göttingen (1892) **38**, 53 pp., 5 pls.

Given the potentials as above, the components of the electric effect of a certain linear displacement and a certain rotation of all the molecules with respect to one of them can be calculated. The calculation shows that

$$p_1 = e_{11}(x_x - y_y) + e_{14}y_z$$
$$p_2 = -e_{11}x_y - e_{14}z_x$$
$$p_3 = 0$$

where p_1, p_2 and p_3 are the components of the resulting piezo-electric moment referred to the unit of volume; e_{11} and e_{14} are the piezo-electric

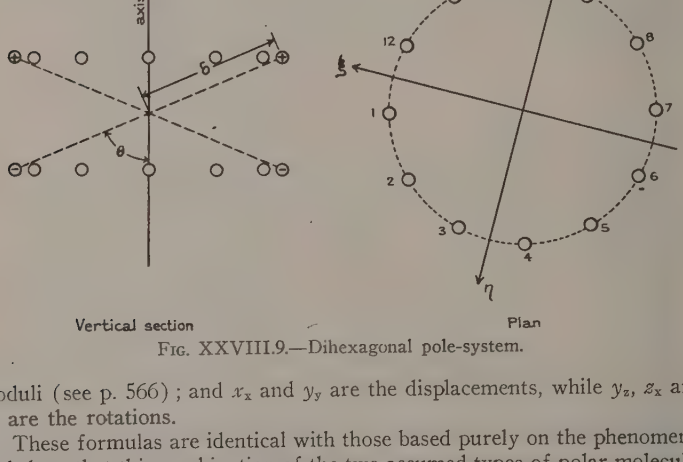


FIG. XXVIII.9.—Dihexagonal pole-system.

moduli (see p. 566); and x_x and y_y are the displacements, while y_z, z_x and x_y are the rotations.

These formulas are identical with those based purely on the phenomena, and show that this combination of the two assumed types of polar molecules is sufficient to explain the piezo-electricity of low-quartz.

The assumed types of so-called molecules will fit the theory of structure presented in Chapter XV, if we identify the trigonal pole-system with a triplet of silicon atoms in a horizontal plane, and the dihexagonal pole-system with the double horizontal layer of triplets of oxygen atoms which exists between two horizontal planes of silicon atoms (see Figs. XIV.4 and 5).

PYRO-ELECTRICITY

Substances which are piezo-electric may also show the phenomena of *pyro-electricity*. This is the name given to the group of phenomena produced by the separation of electric charges on a crystal as a result of changes in its temperature.[32]

[32] See VOIGT, W., *Lehrbuch der Kristallphysik* (1910, Leipzig): pp. 228-261, 299-304, 920-937. POCKELS, F., Encykl. Math. Wiss. (1906) Vol. 5, Pt. 2: pp. 384-386.

A perfectly uniform temperature is very difficult to obtain. The usual effect of trying to warm or cool a crystal is the production of differences of temperature throughout the specimen. The resulting differences in thermal dilatation cause stresses in the specimen, and these, in turn, are capable of giving rise to piezo-electric charges such as would be produced by the equivalent stress applied mechanically. Since the charges are only the secondary result of change in temperature, this type of effect may be called *false pyro-electricity.*

Even when the specimen has been warmed or cooled in such a way that its temperature is uniform throughout, the effect can not be called purely pyro-electric. If the change has taken place under constant pressure, as is nearly always the case in laboratory experiments, there has been a thermal deformation or change in axial ratios (see p. 360). This displacement of the relative positions of the atoms may yield a resultant electric moment, that is, a pyro-electric effect, which could, however, be neutralized by stresses applied externally in such directions as to restore the original dimensions of the specimen. The effect may therefore be called *false pyro-electricity of the second kind.*

The *true pyro-electricity* is the electric moment which remains un-neutralized after the above-described restoration by external stresses. Its very existence has been questioned. Voigt satisfied himself that tourmaline shows true pyro-electricity, but later experiments by Röntgen and by Lindman leave this conclusion open to doubt.

Pyro-electricity in silica

Quartz is the only form of silica which has been studied for pyro-electric phenomena.

The character of the symmetry of both low-quartz and high-quartz precludes the possibility of their exhibiting either true pyro-electricity or false pyro-electricity of the second kind.

All the pyro-electricity of quartz, therefore, is false pyro-electricity of the first kind, due to non-uniform distribution of temperature.

Gibbs [34] deduces from his structure for low-quartz that pyro-electricity is possible in quartz because of the rotation in position of triangular groups of atoms. But since his structure is consistent with the trigonal trapezohedral symmetry of low-quartz the deduction cannot be valid; consideration of the mutual influences of all the atoms which lie near a given atom should eliminate the pyro-electricity completely.

Historical notes

Although phenomena due to pyro-electricity had been observed on imported tourmaline by Dutch jewelry merchants in 1703, the electrical nature of the phenomena was first recognized about 1756, by Aepinus. The name

[34] p. 453 of article cited in XIV, note [8].

"pyro-electricity" was proposed by Brewster[35] in 1824, and it was he, also, who first observed pyro-electricity in quartz.

Many experiments on the pyro-electricity of quartz, mostly of a qualitative rather than quantitative character, were made in the ensuing 60 years by Hankel, Kundt, and others.

In 1880 J. & P. Curie discovered that similar effects could be obtained by stress alone, without the intervention of change of temperature,—the phenomenon later named "piézo-électricité." Friedel & Curie[36] shortly thereafter showed that all the pyro-electric effects observed in quartz can be explained as due to stress, that is, they are special cases of piezo-electricity.

[35] Brewster, D., *Observations on the pyro-electricity of minerals,* Edinburgh Journ. Sci. (1824), **1**: 208-215.

[36] Friedel, C., & Curie, J., *Sur la pyroélectricité du quartz,* Bull. Soc. Mineral. France (1882), **5**: 282-296.

Chapter XXIX. SILICA IN THE MAGNETIC FIELD

Magnetic susceptibility

Any portion of matter, when placed in a magnetic field, becomes a magnet. Most substances (excepting iron, magnetite, and a few other so-called *ferromagnetic* substances) make very weak magnets.

The *magnetization-intensity, J*, produced in a given portion or fragment of such a weakly magnetic substance, is independent of the size and shape of the fragment, but bears a certain ratio to the magnetizing force or *mangetic field intensity, H*. This ratio is called the *susceptibility,* usually denoted by $\varkappa$:

$$\varkappa = \frac{J}{H}$$

Since the magnetization-intensity is independent of shape and size in the non-ferromagnetic substances, it is sometimes convenient to state the susceptibility in terms of mass rather than volume. The *mass-susceptibility* is denoted by $\varkappa'$:

$$\varkappa' = \frac{\varkappa}{d}$$

where d is the density.

In some substances the *magnetic induction, B,* which is equal to $H + 4\pi J$, and which determines the pole-strength of the fragment and the way it will move in the magnetic field, is actually less than H. Such substances are called *diamagnetic*. A fragment of such a substance will tend to move out of a stronger part of a non-uniform magnetic field into a weaker part. B being less than H, J and $\varkappa$ are evidently negative; that is, the susceptibility of a diamagnetic substance is a negative quantity.

For most substances $\varkappa$ is positive and small; such substances are called *paramagnetic*.

In general, $\varkappa$ varies with the field intensity, but for most substances, including silica, the variation is small or inappreciable. An important variation, in crystals, is with the direction in the crystal. A substance of the symmetry of quartz has 2 principal susceptibilities, one parallel to the axis and one perpendicular thereto. $\varkappa$ also varies considerably with the temperature.

Air correction

The foregoing discussion assumes that the fragment is in a vacuum. If immersed in a fluid, its apparent susceptibility depends upon that of the fluid. If it is suspended in air, which is the condition under which such measurements are usually made, its apparent susceptibility is slightly lowered. To change to true $\varkappa$ (or true $\varkappa'$) 0.024×10^{-6} per cc must be added.

Magnetic susceptibility of silica

The modifications of silica are diamagnetic, that is, they have a negative value of $\varkappa$ (and $\varkappa'$). Of the crystalline modifications, only low-quartz has been studied.

The most probable absolute values of $\varkappa$ and $\varkappa'$ are given in Table XXIX.1.

Table XXIX.1.

Most Probable Values of Magnetic Susceptibility for a Random Specimen of Quartz (Values in Vacuum).

Temp. °C	Volume-susceptibility, $10^6\varkappa$		Mass-susceptibility, $10^6\varkappa'$	
	∥ to axis	⊥ to axis	∥ to axis	⊥ to axis
20	—1.21	—1.20	-0.45_7	-0.45_2

The experimental data

The most exact absolute measurements of the magnetic susceptibility of silica are those of Voigt & Kinoshita.[1] The force of displacement on circular plates 2.75 mm in diameter, in a non-uniform field of 1500 to 3500 gilbert per cm, was measured by means of a torsion balance, while the field intensity was measured by the change in resistance of a bismuth spiral.

Only quartz and opal were examined. The results on quartz are:

	Volume-susceptibility in air	Mass-susceptibility in air
Field ∥ to axis	$\varkappa_3 = -1.23_5 \times 10^{-6}$	$\varkappa'_3 = -0.466 \times 10^{-6}$
Field ⊥ to axis	$\varkappa_1 = -1.22_8 \times 10^{-6}$	$\varkappa'_1 = -0.461_4 \times 10^{-6}$

Koenigsberger[2] measured the susceptibility of very pure quartz by the method of suspension in liquids of known $\varkappa$. The plate of quartz was suspended with the principal axis perpendicular to the field of an electromagnet, in a field of 1800 to 2200 gilbert per cm. This gives the value of $\varkappa$ perpendicular to the axis. The value found was -1.20×10^{-6} in air, at 20°. The sensitivity is 0.01×10^{-6} or better.

Specimens of smoky quartz from 2 localities gave the same value as the clear quartz. Several specimens of amethyst were a little less diamagnetic a little Fe_2O_3 or possibly a manganese compound would account for this difference.

Curie[3] measured the susceptibility of quartz in fields of 50 to 1350 gilber per cm and at temperatures of 18 to 430°. His sensitivity seems to have beer insufficient to distinguish between the two constants of quartz. 'The value fo

[1] Voigt, W., & Kinoshita, S., Nachr. K. Ges. Wiss. Göttingen, Math.-phys. K 1907: 123-144. Ann. Physik (1907) (4) 27: 492-514.

[2] Koenigsberger, J., Ann. Phys. u. Chem. (Wied.) (1898) 66: 698-734, p. 725.

[3] Curie, P., Compt. rend. Acad. Paris (1893) 116: 136-139.

both directions and for all temperatures and intensities is $10^6\chi' = -0.441$, or $10^6\chi = -1.17$, with possibly a barely detectable increase accompanying the rise of temperature from 18 to 430°.

Wistrand[4] made 14 determinations on 2 cylinders of quartz in fields of 1430 to 3600 gilbert per cm, using Kelvin's method of weighing the attraction on a long cylindrical specimen with one end in a homogeneous field while the other is in zero field. He obtained the average value $10^6\chi = -1.07$ (in vacuum).

Meyer[5] measured the susceptibilities of a large number of inorganic compounds by weighing the attraction in a non-uniform field of about 10,000 gilbert per cm. The values are relative to mercury, for which $10^6\chi$ was taken as -2.05 at 15°. The result for "natural SiO_2" (presumably quartz), after correction for what appears to be an error in copying, is $10^6\chi' = -0.03$. This is abnormally low, suggesting the possible presence of iron oxide, which is sometimes found included in quartz crystals.

A comparison of the average value of χ' (mass-susceptibility) for quartz follows:

Author	$10^6\chi'$
Voigt & Kinoshita	−0.45
Curie	−0.44
Koenigsberger	−0.44
Wistrand	−0.40
Meyer	−0.03 (?)

Influence of field intensity

There is some uncertainty whether the susceptibility varies at all with the field intensity.

Relative measurements of the difference between the two principal susceptibilities give a sensitive test of this matter, since it is hardly to be expected that both will change by the same absolute amount with changing field.

König[6] measured the turning moment of a magnetic field upon suspended spheres of quartz (2 specimens), and thought that the results showed a real decrease in the difference between the susceptibilities along the vertical and horizontal axes, with increasing field intensity. The average value between 500 and 2800 gilbert per cm was 0.0062×10^{-6}.

Stenger[7] failed to confirm such a variation in 2 series of experiments on a quartz sphere. He found an average difference of 0.0048×10^{-6} in fields ranging from 300 to 1100, with no certain evidence of a change with the field. Curie detected no change between 50 and 1350. Wistrand found no certain evidence of change between 1430 and 3600 gilbert per cm, although his average

[4] Wistrand, G., *Magnetiska susceptibiliteten hos qvarts,* etc., Thesis, Uppsala, 1916, 56 pp.

[5] Meyer, S., Ann. Physik u. Chem. (1899) **69**: 236-263, p. 239.

[6] König, W., Ann. Phys. u. Chem. (Wied.) (1887) **31**: 273-302.

[7] Stenger, F., same (1888) **35**: 331-353, p. 352.

for the higher fields is numerically less, by about 0.005, than the average for the lower fields.

Magnetic retentivity

Fragments of certain substances continue to be magnets even after the original magnetizing field has been removed. Such substances are said to possess *retentivity*. The intensity of magnetization (J) of such a substance after the removal of the original field is called its *remanence*.

According to Tumlirz & Luggin,[8] quartz possesses a small remanence, part of which is of short duration. It shows the effect when the field is parallel to the threefold axis, and again when it is parallel to a twofold axis, being different in opposite directions in the second case. The measurements were made on a plate cut perpendicular to the axis and suspended between the poles of an electromagnet.

As no attention seems to have been paid to the possible effects of piezo-electricity due to unequal heating (see p. 573), I do not believe the evidence can be accepted without further study. Koenigsberger[9] could find no remanent effects even with quartz suspended in a liquid of the same susceptibility, which is the condition of greatest sensitivity. Furthermore, the polar difference along the twofold axis, as found by Tumlirz, adds to the suspicion, since magnetic induction is not a polar property in a substance of trigonal trapezohedral symmetry.

[8] Tumlirz, O., & Luggin, H., Anzeiger K. Akad. Wiss. Wien, M.-N. Cl. (1886) **23**: 93-94.

[9] Article cited.

Part 7. Silica in the Periodic Electromagnetic Field

Chapter XXX. REFRACTION

Radiant energy

One of the greatest accomplishments of physical science during the latter half of the nineteenth century was the proof of the essential unity of various kinds of radiation which at first seemed very different one from another.

All experimental data are now in agreement with the principle that X-rays, light, radiant heat, and electromagnetic radiation ("radio waves") are qualitatively alike and differ only in a measurable quantitative way, usually expressed in terms of speed and wave-length, or the *frequency* of a vibration. In a vacuum, all these different-named forms of radiant energy are alike in their speed and their mode of transmission.

We customarily classify them roughly by their frequency, or by their wave-length in a vacuum, which is inversely proportional to the frequency. Figure XXX.1 shows graphically the range of frequencies and wave-lengths covered by the usual descriptive names for radiant energy. A sine function of the logarithm of the wave-length is used as the linear unit in the diagram, in order to spread out the scale in the vicinity of the visible spectrum.

Since the frequency of a given kind of vibration is invariable while the wave-length and speed vary reciprocally to one another, it seems most logical to describe any given kind of radiation in terms of its frequency. The custom has become almost universal, however, of stating frequency in terms of wave-length. Furthermore, for the sake of experimental precision, because practically all the measurements are made in air, it is the accepted custom to state wave-lengths as if in dry air at 15°C and 760 mm standard pressure, corrections being made for the small departures from this standard condition met with in laboratory practice.

Character of the vibration

Not only are all the wide-ranging frequencies of radiant energy alike in character, but their phenomena are all equally explainable in terms of the properties of a periodically varying electromagnetic field. The imaginary vibration, then, is recognized to consist of two vectors: an electric vector, and a magnetic vector, whose directions are definitely related to the *wave-surface*. The wave-surface is the surface passing through all the points at which, after a definite time, is felt the homogeneous effect emanating from a luminous or radiating point.

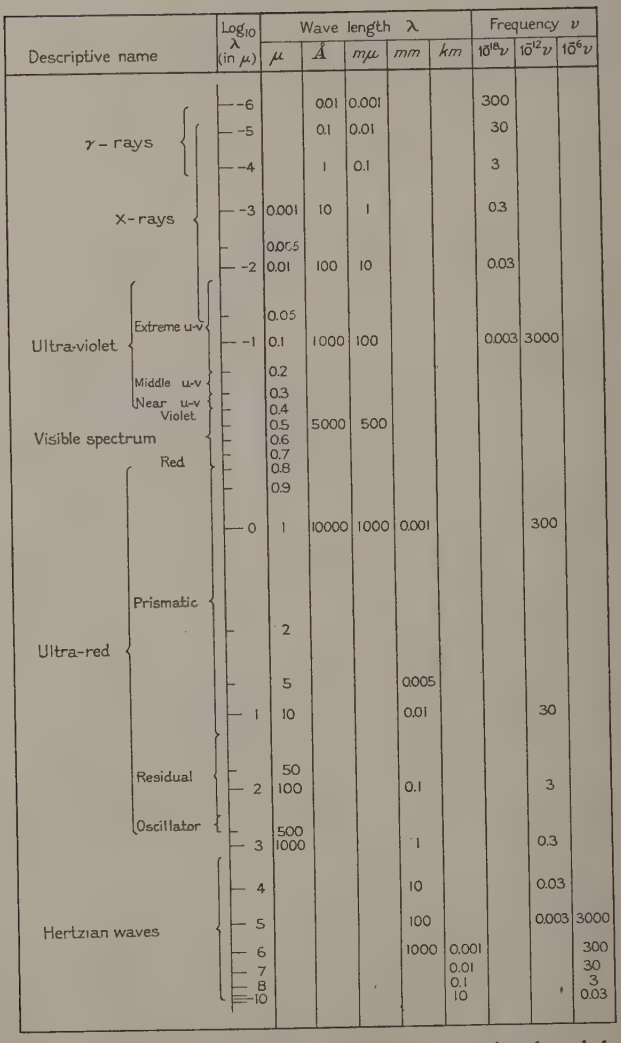


FIG. XXX.1.—Graphical comparison of the ranges of wave-length and frequency covered by the usual descriptive names for radiant energy.

Their electromagnetic character thus makes this chapter, which introduces the "optical" properties, follow naturally upon the chapters dealing with the electric and magnetic properties (XXVI to XXIX).

Purity of radiation

As the chemist distinguishes between a pure substance and a mixture, so the physicist recognizes radiation to be sometimes homogeneous, sometimes heterogeneous. The general classification on the basis of frequency may therefore be supplemented by the practical distinction between:

(A) *Monochromatic* radiation, which is of a single frequency (single wave-length, single physical color); and

(B) *Polychromatic* radiation, a complex vibration from which a large number of kinds of monochromatic radiation can be obtained, for example, by means of a grating or prism.

Polarization

Radiant energy of a given frequency, but from two different sources, may look or feel exactly the same, and yet produce very different physical effects in an optical instrument or in a crystal. These differences have proved, on the basis of innumerable experiments, to be explainable by the assumption that there exist different *types of vibration* in radiant energy.

Monochromatic radiation may be:

(a) *Plane-polarized.* The hypothetical vibration or vector-magnitude (the electric vector), which constitutes the radiation, is confined to one plane only, as the radiation progresses through a vacuum.

(b) *Circularly-polarized.* The vibration takes place in a circular path, which may be clockwise (right) or counter-clockwise (left) as seen by an observer toward whom the radiation is coming.

(c) *Elliptically-polarized.* This is the most general type of polarized radiation, since it includes (1) and (2) as special cases. Circularly-polarized radiation may be considered as the limiting case of an elliptically-polarized radiation when the two axes of the ellipse become equal; while plane polarization results when one axis of the ellipse becomes infinitesimally small compared with the other.

(d) *Non-polarized.* Within a very short interval of time the transverse vibrations occur in all possible directions across or around the normal to the wave-surface.

Polychromatic radiation (including white) is likewise recognized as being non-polarized, elliptically-polarized, circularly-polarized, or plane-polarized; or as a mixture of polarized and non-polarized.

Matter and radiant energy

Radiant energy, after passing from a vacuum into a material substance such as a quartz crystal, finds itself *retarded* in its speed of transmission.

As a result of this retardation, the energy passing initially from a vacuum into the quartz or from the quartz into some other substance, is in part *reflected,* while the rest is *refracted* and is transmitted at a different speed.

Both the reflected and the refracted portions, in their temporary or continuous progression into the quartz crystal, undergo in general a *change in the manner of vibration.* The energy, furthermore, is partly *scattered* and partly *absorbed.*

The absorbed portion may be wholly converted into heat (vibration of atoms or atom-groups) ; or it may be only partly converted into heat while the remainder is transformed or stored and is at once or later *re-radiated* at a different frequency (phenomena of luminescence).

If the frequency or type of the radiation and its manner of vibration is known, the above-mentioned effects can be quantitatively predicted in any given case with the help of the so-called optical constants or *radiational constants* of the substances involved. The values of these constants for the forms of silica will be our next concern.

The forms of silica are transparent to some frequencies, and opaque to others; and the phenomena produced in silica plates, in lenses, in prisms, in fragments of all shapes, by the different kinds of monochromatic, polychromatic, and white radiation, are extremely varied and complex. Nevertheless, nearly all the phenomena can be completely described and specified on a foundation of general principles built up by the labors of mathematical and experimental physicists during two hundred years. It is the purpose of the next few chapters to show how the properties of silica fit into this foundation.

In defining the most of these constants and describing the phenomena of which the constants are a quantitative measure, we need not hold to any hypothesis regarding the nature of radiant energy or its mode of transmission. The so-called "vibration" may be considered simply as a conventional way of describing a lot of phenomena which have been found to lend themselves well to this kind of a convention.

We know now that some of the phenomena of radiant energy cannot be completely described in terms of vibrations and waves, but require a theory which describes the energy in terms of separate units or *quanta,* the so-called "quantum theory". Our systems of description are therefore, at the moment, in a state of change and uncertainty. Refraction and reflection, however, which are our present concern, can be perfectly well described in terms of vibrations and the wave theory.

Refractive constants of silica at room temperature

For convenience of reference, the most useful refractive constants of silica, both fundamental and secondary, are given in Table XXX.1. The meaning of each constant is more fully discussed in later paragraphs.

TABLE XXX.1.

THE MOST USEFUL FUNDAMENTAL AND SECONDARY RADIATIONAL CONSTANTS OF SILICA AT ROOM TEMPERATURE.

		Low-quartz	Low-tridymite	Low-cristobalite	Vitreous
Indices of refraction for sodium light	n_α n_β n_γ	1.544 (n_ω) $n_\beta = n_\alpha$ 1.553 (n_ϵ)	1.469 1.47 1.473	1.484 near 1.487 1.487	$n_\alpha = n_\beta = n_\gamma$ $n_\beta = n_\alpha = n_\gamma$ 1.459
Birefringence for sodium light	$(n_\gamma - n_\alpha)$	0.009	0.004	0.002	0
Constringence	.....	{for o 69.9 {for e 68.7	.....	.....	67.6
Optical character	.....	Positive (prolate)	Positive	Negative	
Optical orientation	.....	$c = n_\gamma$	.....	.....	
Optical character of elongation	.....	Positive	Negative	.....	
Optic axial angle	$2V_\gamma$	0	35 to 43°	Over 90°	
Apparent optic axial angle	$2E_\gamma$	0	56 to 66°	Over 90°	
Optical rotatory power for sodium light	ρ	21.72° per mm	Unknown	Unknown	0.000°

The index of refraction

The first and most important effect of matter on radiant energy is the retardation of its speed, resulting in *refraction* and *reflection*. This effect is stated quantitatively by means of the *index of refraction*. The index of refraction of a substance for a definite radiation is defined as the *ratio of the speed of the radiant energy in a vacuum to its speed in the substance*.

The index as defined above is the so-called "index in vacuum" or *absolute* index. What is usually measured experimentally, however, is not the absolute index but the *index in air* at room temperature and atmospheric pressure; that is, the ratio of the speed of radiant energy in air to its speed in the substance. This is the constant which is most directly related to the experimental measurements, just as specific gravity is more directly related to the experimental data than true density (see XVIII). The index in air can be converted into absolute index by multiplying by the absolute index of air.

The symbol n will be used for absolute index, or, in general, for any refractive index if the question of air corrections need not be taken into account. When a distinction is necessary, the index in air will be represented by N.

The magnitude of the difference is illustrated by the following example: if a substance's index of refraction in air at 20° and normal pressure, for yellow sodium light, is $N = 1.500\ 000$, then its true index at 20°, for sodium light, is $n = 1.500\ 408$.

The retardation of the energy, and hence the index of refraction, depends upon the number and state of motion of the electrons, atoms, and atom-groups met with along the path, and is therefore influenced by the following variables:

(1) The frequency of the radiation,
(2) The direction of the radiation,
(3) The temperature of the substance.
(4) The state of stress and strain of the substance.

Relation of the refractive index to the frequency

The speed of radiant energy in a vacuum is the same for all frequencies. But in a solid, liquid, or gas the speed varies with the frequency in a manner to be determined experimentally for each substance. This variation is the cause of the phenomena of *dispersion*. A statement of the index of refraction of a substance, therefore, needs to be accompanied by a statement of the frequency or physical color of the radiation in which it was measured.

Relation of the refractive index to the direction

Birefringency

The radiant energy entering a fragment of a substance such as quartz is not only retarded; it also undergoes changes in its manner of vibration. In general the following important effects result:

(1a) The radiation is propagated within the substance by *two* distinguishable sets of waves instead of the original *one;*

(1b) The radiation of both of these sets of waves is *polarized,* with vibration-directions in planes ⊥ to one another.

Substances showing these effects are known as "doubly refracting" or ***birefringent.***

(2) The radiation may emerge from the other side of the fragment vibrating in directions which are not deducible from the principles of birefringency alone. Substances showing this effect are known as "optically active" or ***rotatory.***

Birefringent biaxial substances. Low-tridymite and low-cristobalite

In a birefringent substance which is not rotatory the propagation of radiant energy, as already mentioned, is by means of two polarized waves. For a given frequency the phenomena can be completely expressed in terms of three constants, namely, the three velocities V_1, V_2, and V_3 of waves vibrating parallel to three mutually perpendicular axes in the crystal, known as its "axes of optical elasticity". The position of these axes is in most crystals determined by the symmetry, while in some it constitutes an additional characteristic constant of the substance to be determined experimentally.

Suppose that the reciprocal of the velocity of propagation of a disturbance vibrating parallel to any given direction be represented by a line, measured off in the direction of the vibration, and bisected by a given fixed point. In every plane passing through this fixed point there is one reciprocal velocity which is a maximum, and another, perpendicular to the first, which is a minimum. The facts of crystalline birefringence have demonstrated that the terminal points of all such maxima and minima lie on a ***triaxial ellipsoid.***

The triaxial ellipsoid is the general form of surface which is represented by an equation of second degree; it might be described in petrologic language as an ellipsoid having the shape of an elongated water-rounded pebble of flagstone; to the chemist or ceramist it might be described as the shape one would obtain by rounding off the corners and edges of a match-box or a brick so that their principal cross-sections would become elliptical. Similar rounding of a square post or a square tile would produce ellipsoids of revolution, not triaxial ellipsoids.

The equation of this triaxial ellipsoid is

$$\left(\frac{V_1}{V}\right)^2 x^2 + \left(\frac{V_2}{V}\right)^2 y^2 + \left(\frac{V_3}{V}\right)^2 z^2 = 1$$

where V is the velocity of radiant energy in a vacuum. But the ratio of V to the velocity of radiant energy within a substance is what is called an index of refraction (see p. 581); hence the three ratios

$$\frac{V}{V_1} = n_\alpha \qquad \frac{V}{V_2} = n_\beta \qquad \frac{V}{V_3} = n_\gamma$$

are called the *principal indices of refraction* of the birefringent substance, and the ellipsoid is called the *index ellipsoid*. It is customary to call the smallest of the three indices n_α, and the largest, n_γ. The whole quantitative statement of the refractive phenomena (excepting in some instances their relation to the symmetry) is contained in these three indices.

The substance is called *biaxial* because it contains two directions,[1] the *optic axes* or "binormals," along which plane waves are transmitted with one uniform velocity, whatever the direction of the vibrations in the wave-front. They are directions along which one wave only is propagated, instead of two as is generally the case. This is simply a geometrical fact following from the considerations in the foregoing paragraphs, although historically it was one of the principal experimental facts from which the mathematical doctrine of birefringency has grown.

It follows mathematically that the wave-front or ray-surface which would be formed by radiation starting from a point within the substance has the form of two closed surfaces or sheets, one inside the other, which touch each other at four points, and whose combined cross-sections on the principal planes of the index ellipsoid are ellipses and circles (Fig. XXX.2). The outer sheet has the general shape of a smooth potato with four shallow eyes or dimples in its surface.[2]

Low-tridymite and low-cristobalite belong in the class of birefringent biaxial crystalline substances, and therefore possess 3 principal indices of refraction for a given frequency. It is not known whether or not they are rotatory.

Employing the conventions as to axes and relative velocities shown in Figure XXX.2, if the angle between an optic axis and the Z-axis is less than 45°, the substance is called *optically positive*; if greater than 45°, *optically negative*. Low-tridymite is thought to be positive, and low-

[1] It is to be noted that an optic axis is a *direction*, and not a fixed line, in the crystalline substance.

[2] For a more complete discussion of the formal theory of birefringency see:
POCKELS, F., *Lehrbuch der Kristalloptik* (1906, Leipzig) pp. 18-92.
FLETCHER, L., *The optical indicatrix* (1892, London).
ROSENBUSCH & WÜLFING, *Mikroskopisch Physiographie der Mineralien*, 5th Ed. (1921-1924, Stuttgart) Vol. I, Pt. I, pp. 74-127.
SCHUSTER, A., *Theory of optics* (1909-1924, London) pp. 168-194.

cristobalite, negative; but the evidence is not very clear, for the differences between the three indices in each case are not very large.

Birefringent uniaxial substances. Low-quartz

Let us suppose that by changing the temperature or composition of a birefringent biaxial non-rotatory substance we can bring the intermediate index n_β nearer and nearer to n_α until the two are equal for a given frequency. This means that in the cross-sections in Figure XXX.2 the value of V_2 is made to equal V_1. It is evident that the two-sheet wave-front will become a sphere enclosing within it an ellipsoid of revolution or prolate *spheroid,* and that the angle between the two optic axes will close up to 0°, the two axes becoming coincident. The cross-sections would then appear as in Figure XXX.3.

A similar result would be attained by making n_β approach n_γ instead of n_α, except that the spheroid would then be oblate instead of prolate, and would be outside instead of inside the sphere.

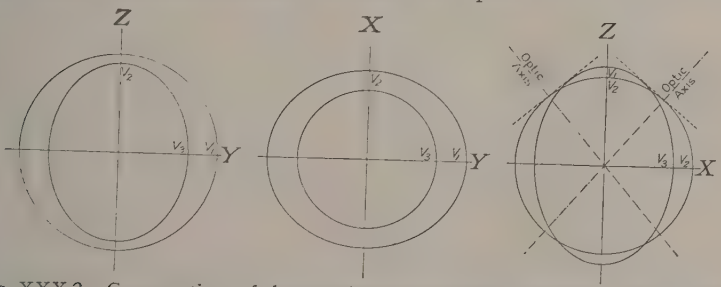


FIG. XXX.2.—Cross-sections of the two-sheet wave-front of radiation which is being propagated in a birefringent *biaxial* substance.

Substances having wave-surfaces of these forms for all frequencies are called birefringent *uniaxial,* because they contain only *one* direction in which both waves progress with the same velocity. Except for the relatively small deviations due to its rotatory power, low-quartz is birefringent uniaxial.

This is not a complete statement of the refractive character of quartz, however, as it does not show whether $n_\beta = n_\gamma$ or $n_\beta = n_\alpha$. When $n_\beta = n_\alpha$, the substance is called "optically prolate"[3] or *positive;* when $n_\beta = n_\gamma$, "optically oblate" or *negative.* Low-quartz is a birefringent, positive (prolate), uniaxial substance.

High-quartz and the high-tridymites are also birefringent positive uniaxial.

The rays corresponding to the two wave-fronts in a birefringent uniaxial substance are sometimes distinguished by the terms "ordinary

[3] SCHUSTER, A., *Theory of optics* (1909-1924, London) p. 184.

ray" (for the spherical ray-surface) and "extraordinary ray" (for the spheroidal ray-surface). The indices of refraction are, correspondingly, indicated by n_o or n_ω (ordinary) and n_e or n_ϵ (extraordinary). In a positive substance $n_\epsilon > n_\omega$ and in a negative substance $n < n_\omega$.

In low-quartz, high-quartz, and the high-tridymites n_ϵ is equivalent to n_γ of the general case, and n_ω to n_α.

Unirefringent or isotropic substances. Vitreous silica

Birefringent *uni*axiality, as just shown, is derived from birefringent *bi*axiality by the approach of the index n_β to equality with n_α or n_γ. Similarly, if the remaining index (n_γ or n_α) approaches the one which has merged with n_β, finally becoming equal (for a given frequency) to the merged pair, the substance will have only one index of refraction, n. The two sheets of the wave-front merge into one, a *sphere*.

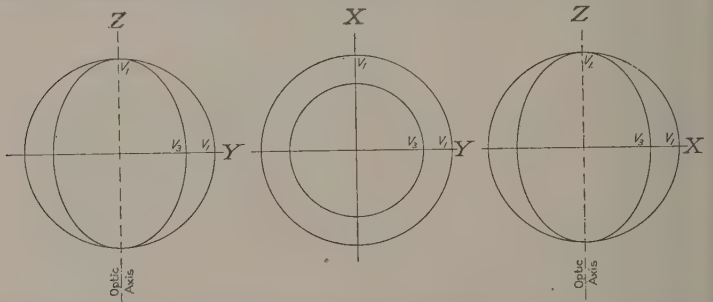


FIG. XXX.3.—Cross-sections of the two-sheet wave-front of radiation which is being propagated in a birefringent *positive uniaxial* substance. Derived from the general case in Figure XXX.2 by making $V_2 = V_1$.

A substance in which this is true for all frequencies is called "monorefringent," "unirefringent," or *optically isotropic*. In type, vitreous silica and high-cristobalite are optically isotropic.

RELATION OF THE REFRACTIVE PROPERTIES TO THE SYMMETRY

In the foregoing paragraphs only passing mention has been made of the crystallographic axes of the substances whose optical properties were being considered. Only the numerical magnitudes of the three indices n_α, n_β, and n_γ (the three axes of the index-ellipsoid) were taken into account. A complete statement of optical properties, however, would seem to require the further specification of the orientation of the index-ellipsoid with respect to the geometrical axes employed in describing the symmetry of the crystal.

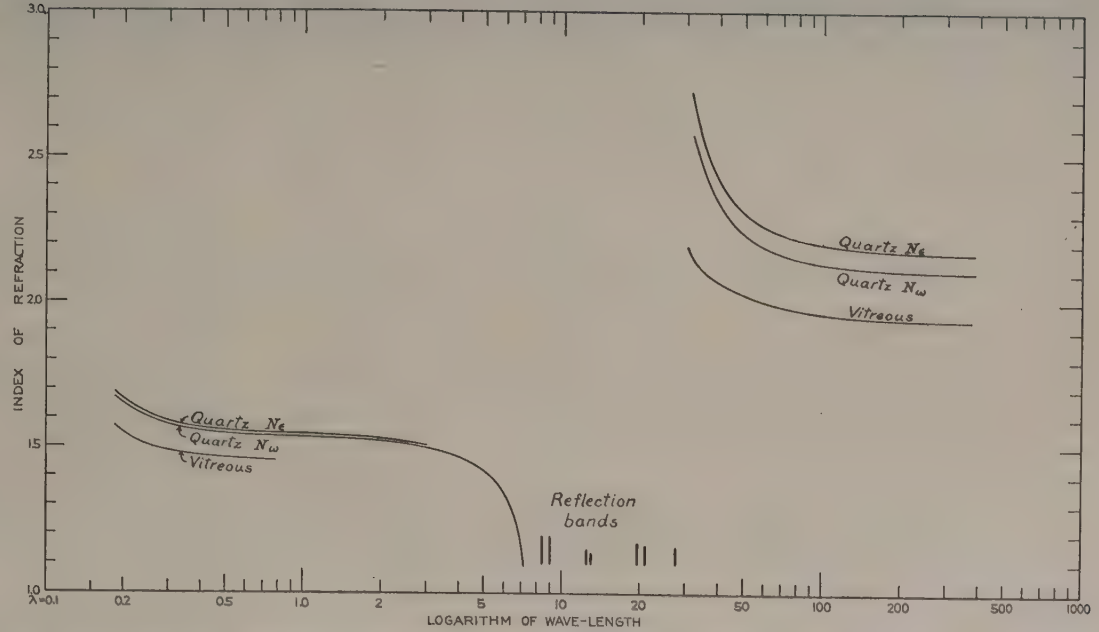


FIG. XXX.4.—Indices of refraction of quartz and vitreous silica at 18°C, as related to wave-length, over the range from 180 mμ to 300 μ.

For the modifications of silica, this additional requirement is quickly disposed of.

Since high-cristobalite has no optic axis, its wave-front, a sphere, needs no orienting.

In low-quartz, high-quartz, and the high-tridymites the symmetry determines completely the position of the index-ellipsoid. The single optic axis of each modification coincides with its principal crystallographic axis, and the refractive properties of these four are thus completely specified by giving the values of n_ϵ and n_ω. The same will be true for low-tridymite if its symmetry proves to be tetragonal.

In low-cristobalite and low-tridymite, furthermore, assuming that their symmetry is orthorhombic, but not lower, the axes of the index-ellipsoid must coincide with the axes of the crystal; but this does not complete the description. The axes of the ellipsoid are unequal, hence it must be stated which crystallographic axis coincides with n_α and which with n_γ.

Because of the doubt still existing as to the symmetry of these two modifications, this final specification of the position of the ellipsoid can not be given with certainty.

If low-tridymite and low-cristobalite should prove to be monoclinic or triclinic, as has been suspected by some crystallographers, then additional constants, consisting either of one or of three angles, will be necessary in order to place the index-ellipsoid with reference to the axes of the substance.

Indices of refraction of silica at room temperature

The most probable values of the refractive indices of quartz and vitreous silica at 18° and at various frequencies are presented in Table XXX.2. The data are represented graphically in Figures XXX.4 and 5.

The indices of tridymite and cristobalite are known only for sodium light, and the most probable values have already been given in Table XXX.1.

The wave-lengths adopted for specific radiations in Table XXX.2 are selected values in international units as listed by Kayser[4] in a table received just in time to permit of a general revision of the data. These values have been supplemented where necessary by Volumes 6 and 7 of his general work.[5] The wave-lengths are uniform through all the tables of precise data in this and subsequent chapters, wherever characteristic radiations were used which I could identify with certainty. The solar wave-lengths are Rowland's, corrected to international units. This retabulation of all wave-lengths makes the calculations and comparisons consistent throughout, although it is possible that

[4] Kayser, H., *Tabelle der Hauptlinien der Linienspektra aller Elemente* (1926, Berlin), 198 pp.

[5] Kayser, H., *Handbuch der Spektroscopie* (1900-1924, Leipzig), especially Vol. 6 pp. 893-1033.

TABLE XXX.2.

MOST PROBABLE VALUES OF THE REFRACTIVE INDICES OF QUARTZ AND VITREOUS SILICA AT VARIOUS FREQUENCIES, AT 18°, IN AIR AT SAME TEMPERATURE.

Radiating element	Wave-length in air at 15° mμ	N_ω Quartz	N_ϵ Quartz	N Vitreous
Al	185.467	1.675 78	1.689 97	1.574 36
Al	193.583	1.659 99	1.673 43	1.559 99
Au	200.06	1.649 27	1.662 27	
Zn	202.55	1.645 57	1.658 42	1.547 27
Au	204.448	1.642 88	1.655 62	
Au	211.07	1.634 32	1.646 71	
Cd	214.439	1.630 39	1.642 62	1.533 86
Cd	219.462	1.624 97	1.636 98	1.529 07
Cd	226.503	1.618 18	1.629 92	1.523 08
Cd	231.288	1.614 01	1.625 59	1.519 41
Au	242.796	1.605 25	1.616 50	
Au	250.329	1.600 32	1.611 39	1.507 45
Cd	257.304	1.596 22	1.607 14	1.503 79
Al	263.155	1.593 09	1.603 89	
Cd	274.867	1.587 52	1.598 13	1.496 17
Au	291.358	1.580 98	1.591 36	
Sn	303.412	1.576 955	1.587 20	1.485 94
Au	312.279	1.574 33	1.584 485	
Cd	325.253	1.570 915	1.580 95	
Cd	340.365	1.567 47	1.577 385	1.478 67
Al	358.68	1.563 915	1.573 705	
Ca	396.848	1.558 13	1.567 72	1.470 61
Hg	404.656	1.557 156	1.566 71	1.469 68
H	410.174	1.556 502	1.566 031	
H	434.047	1.553 963	1.563 405	1.466 90
Hg	435.834	1.553 790	1.563 225	1.466 75
Cd	467.815	1.551 027	1.560 368	1.464 35
Cd	479.991	1.550 118	1.559 428	1.463 55
H ("F")	486.133	1.549 683	1.558 979	1.463 18
Cd	508.582	1.548 229	1.557 475	1.461 91
Mg ("b_1")	518.362	1.547 651	1.556 877	
Cd	533.85	1.546 799	1.555 996	1.460 67
Hg	546.072	1.546 174	1.555 350	1.460 13
Hg	579.066	1.544 667	1.553 791	
He	587.563	1.544 316	1.553 428	
Na (mean)	589.29	1.544 246	1.553 355	1.458 45
Au	627.82	1.542 819	1.551 880	
Cd	643.847	1.542 288	1.551 332	1.456 74
H ("C")	656.278	1.541 899	1.550 929	1.456 40
He	667.815	1.541 553	1.550 573	
Li	670.786	1.541 466	1.550 483	
He	706.520	1.540 488	1.549 472	1.455 17
He	728.135	1.539 948	1.548 913	
K	766.494	1.539 071	1.548 005	
Rb	794.763	1.538 478	1.547 392	1.453 40
O	844.67	1.537 525	1.546 40	
	1000.00	1.535 03	1.543 81	
Hg	1014.06	1.534 83	1.543 60	
He	1083.03	1.533 87	1.542 60	
	1200.00	1.532 32	1.540 98	
	1300.00	1.531 02	1.539 62	
	1400.00	1.529 72	1.538 26	

TABLE XXX.2.(*Continued*)

Radiating element	Wave-length in air at 15° mμ	N_ω Quartz	N_ϵ Quartz	N Vitreous
Hg	1529.61	1.528 00	1.536 46	
	1600.00	1.527 03	1.535 45	
	1800.00	1.524 13	1.532 42	
He	2058.20	1.519 98	1.528 14	
	2500.00	1.511 56	1.519 5	
	3000.00	1.499 62	1.507 0	

in individual instances the original author had more accurate data than I have used. The best of the data on quartz, however, are of higher precision than many of the wave-lengths that are available.

The experimental data on which Table XXX.2 is based will be considered more fully in later pages.

THE EXPERIMENTAL DATA ON THE REFRACTIVE INDEX OF VITREOUS SILICA

The data on quartz are so abundant and varied that they will be considered in a separate chapter (XXXI). In the present chapter we shall take up the data on vitreous silica, tridymite, and cristobalite.

As in previous chapters, we are interested to know first what degree of constancy can be expected when precise measurements are made on different specimens which are considered equally representative of the substance.

That vitreous silica can be made uniform and with reproducible properties has been shown by Gifford & Shenstone.[6] Two prisms were made. One, with faces 41 × 32 mm, was built up by Shenstone & Lacell from hundreds of small rods of vitreous silica, made from quartz by fusion in an oxy-gas flame, with thorough heating to the highest temperature in order to drive off traces of sodium and lithium which were present in the quartz used. The completed mass was then heated in a furnace above 1750°C. A second prism, 56 × 38 mm, was made by cementing together 4 flat slabs made by the firm of Baird & Tatlock. A comparison of the two gave the following results for solar lines D and F, at 15°:

	N_D	N_F
Single prism	1.458 477 2	(Not stated)
Compound prism	1.458 483 0	(Not stated)
Difference × 10^6	5.8	10.3

The second prism, composed of four slabs cemented together, furnishes a good test of the reproducibility of the glass as made by the same

[6] GIFFORD, J. W., & SHENSTONE, W. A., Proc. Roy. Soc. London (1904) 73: 201-208.

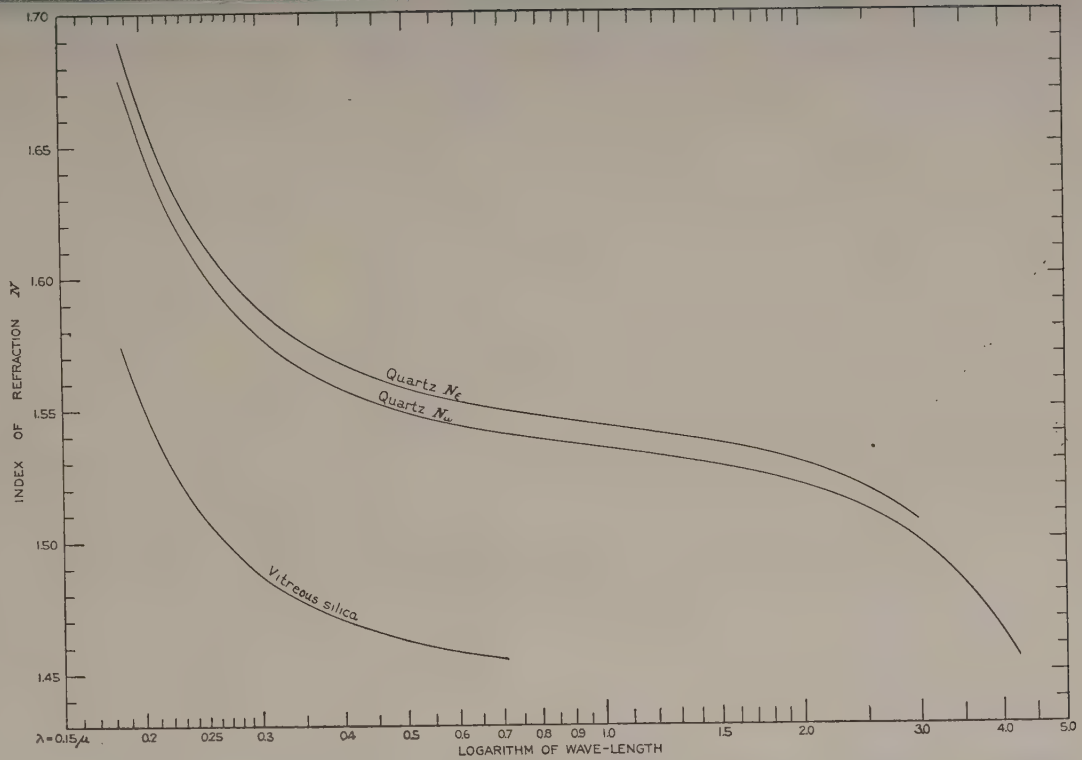


FIG. XXX.5.—Indices of refraction of quartz and vitreous silica at 18°C, as related to wave-length, over the range from 185 to 5000 mμ.

workman. The spectral lines furnished by this prism were sharp, the D line of sodium being resolved into its two components, while a similar compound prism made of four pieces of borosilicate flint 0.364, taken from different parts of the same melting, caused the D line to appear as a bundle of 6 lines. The vitreous silica was thus much more uniform in properties than the optical glass.

Here are five pieces of vitreous silica with indices uniform to about 1 in the fifth place, although made by two different workers. This is a very high degree of reproducibility. The fact should be noted, however, that the method of making the glass was the same, namely, fusion of clear crystals in the oxy-gas or oxy-hydrogen flame.

TABLE XXX.3.

BEST MEASUREMENTS OF THE REFRACTIVE INDEX OF VITREOUS SILICA FOR SODIUM LIGHT (D).

Investigator	Index N_D
Gifford (1904)	1.458 48
Trommsdorff (1901)	1.458 43
Riedel (1903)	1.458 48

A much larger difference was found by Schulz [7] between two specimens measured on an Abbe-Czapski total-reflectometer reading to 20″. The results are:

	N_D
Vitreous silica made by Heraeus	1.4589
Vitreous silica made by fusion of crystals from Minas Geraes	1.4584
Difference	0.0005

No other direct comparisons between two or more specimens are available.

The most accurate of the measurements (in sodium light) by different investigators are in good agreement, as will be seen in Table XXX.3. (See p. 595 for further description.)

TABLE XXX.4.

COMPARISON OF LESS ACCURATE DATA ON THE REFRACTIVE INDEX OF VITREOUS SILICA FOR SODIUM LIGHT.

Investigator	Index N_D	Reference
(Best value)	1.458 5	
Watson (1890)	1.458 7	Phil. Mag. (1890) **30**: 116.
Brun (1896)	1.458 8	Arch. sci. phys. nat. (1896) **2**: 657.
Dufet (1901)	1.458 8	Soc. Franc. Physique 1901.
Abbe (1903)	1.458 5	Int. Kong. Ang. Chem. 1903, **1**: 708.
Schulze (1904)	1.455 0	Ann. Physik (1904) **14**: 387.
Wright (1906)	1.460	Am. J. Sci. (1906) **22**: 297.

Other measurements, of lower accuracy, are compared in Table XXX.4. It will be seen that the measurements by Watson, by Brun, by Dufet, and by Abbe are in good agreement with the most probable value; but Schulze's, made

[7] p. 489 of article cited in XIX, note [36].

at 21.9° on a bar by the Kohlrausch total-reflectometer, is 0.003 low; while Wright's, made on a polished surface of Day & Shepherd's glass (see p. 807) by means of an Abbe refractometer, is 0.002 high. The latter deviation may have been due to the somewhat unsatisfactory material obtained in the early experiments, for Merwin[8] has since found that a cloudy portion of this same glass, perhaps colored by reduced silicon, has an index of 1.460, while the clear part has the normal index near 1.459.

From what we have already learned of the properties of fused silica, it seems not unlikely that there are real differences in its index following some such variables as the maximum temperature to which the liquid has been heated, or the rate of cooling of the glass. Small amounts of alkali or alkali-earth impurities may also have a considerable effect. Nevertheless it is hard to believe that the variation in clear vitreous silica can be as much as 0.003. Furthermore, basic impurities would raise the index, so that Schulze's low value remains unexplained. The question of variability is open for further experiment.

Gifford's and Trommsdorff's curves of refractivity against frequency differ consistently in the range 210 to 500 mμ, to a maximum amount of about 0.0005. (See Fig. XXX.6.)

Data on the relation of refractivity to frequency

The best measurements are those of Gifford & Shenstone,[9] made on two prisms which agreed within $6 / 10^{-6}$ at the D line (see p. 592).

The measurements are at the same 33 frequencies as for quartz (see XXXI). They are estimated to be certainly correct in the fourth decimal place; in almost all cases the error does not exceed 1 in the fifth place and in many does not exceed 5 in the sixth. The data are thus only a little less accurate than those for quartz. The lower accuracy is ascribed to the presence of numerous fine bubbles. The complete results are included in Table XXX.5.

Of equally wide range and nearly as high precision are the measurements of Trommsdorff,[10] made at 36 frequencies on a prism of silica melted by Herschkowitsch at Jena. These results also are given in Table XXX.5.

Riedel[11] measured the index at 5 solar frequencies. The measurements were made in the Zeiss works at Jena.

Watson[12] measured at 5 flame frequencies with a 57-degree prism.

Rinne[13] determined the index of vitreous silica at 18°C for 6 visible frequencies, using the method of minimum deviation in a prism, with a goniometer reading to 2 seconds. The precision is about 0.0001.

The results of Riedel, Rinne, and Watson are assembled in Table XXX.6.

[8] Information from Dr. Merwin.

[9] Article just cited, also article cited in XXXI, note [26].

[10] Trommsdorff, H., *Die Dispersion Jenaer Gläser im ultravioletten Strahlengebiet*, Inaug.-Diss. Jena 1901, 39 pp., 1 pl.

[11] See Herschkowitsch, M., article cited in V, note [20].

[12] Publ. by Boys, C. V., Phil. Mag. (1890) **30**: 116-118.

[13] Rinne, F., *Beitrag zur optischen Kenntnis der kolloidalen Kieselsäure*, Neues Jahrb. Mineral. (1914) Beil.-Bd. **39**: 388-414.

TABLE XXX.5.

EXPERIMENTAL DATA ON THE REFRACTIVE INDEX OF VITREOUS SILICA AT ROOM TEMPERATURE, IN AIR AT SAME TEMPERATURE. GIFFORD, 1902-1910; TROMMSDORFF, 1901.

Radiation	Wave-length mμ	*N*, Gifford	*N*, Trommsdorff
Al	185.467	1.574 3	1.574 64
Al	186.290		1.572 68
Al	198.58	1.559 98	1.560 71
Al	198.98	1.551 990	1.552 04
Zn	202.55	1.547 21	1.547 29
* Zn	206.31	1.542 71	1.542 69
Zn	210.05 †	1.538 547	1.538 57
Cd 26	214.439	1.533 898	1.533 86
Cd 25	219.462	1.529 103	1.529 11
Cd 24	226.503	1.523 053	1.523 18
Cd 23	231.288	1.519 373	1.519 54
Cd 22	232.115		1.518 90
Cd	232.927		1.518 34
*§ Ag	244.53	1.510 96	
Zn	250.20		1.507 62
Zn	255.795		1.504 72
Cd 18	257.304	1.503 707	1.503 97
Cd 17	274.867	1.496 131	1.496 34
Cd 15	298.062		1.488 59
Sn	303.412	1.486 881	
‡ Cd	325.253		1.481 83
* Zn	330.28	1.480 610	
Cd 11	340.365		1.478 77
* Cd 10	346.69		1.477 66
Cd	353.567		1.476 45
¶ Cd 9	361.25	1.475 112	1.475 03
Al	394.403		1.470 86
Al	396.154	1.470 542	1.470 69
Cd 8	398.82		1.470 28
Hg	404.656	1.469 675	
Hγ	434.047	1.466 850	1.466 90
Hg	435.834	1.466 741	
Cd 7	441.568		1.466 30
Cd 6	467.815		1.464 33
Cd 5	479.991	1.463 571	1.463 57
Hβ	486.133	1.463 165	
Cd 4	508.582	1.461 903	1.461 90
* Fe	526.995	1.460 995	
Cd 3	533.85		1.460 67
Cd 2	537.89		1.460 47
Hg	546.072	1.460 155	
* Pb	560.88	1.459 507	
* Na	589.29	1.458 477	1.458 43
Cd 1	643.847	1.456 771	1.456 73
Hα	656.278	1.456 415	1.456 40
Li	670.786	1.456 072	
* He	706.520	1.455 180	
* K	768.19	1.453 892	
Rb	794.763	1.453 398	

* Mean intensity.
† Doubtful wave-length; see footnote † to Table XXXI.6.
‡ Not Cd 12; see footnote †† to Table XXXI.6.
§ Wrong identification; see footnote ‡ to Table XXXI.6.
¶ Probably mean intensity of 3 lines.

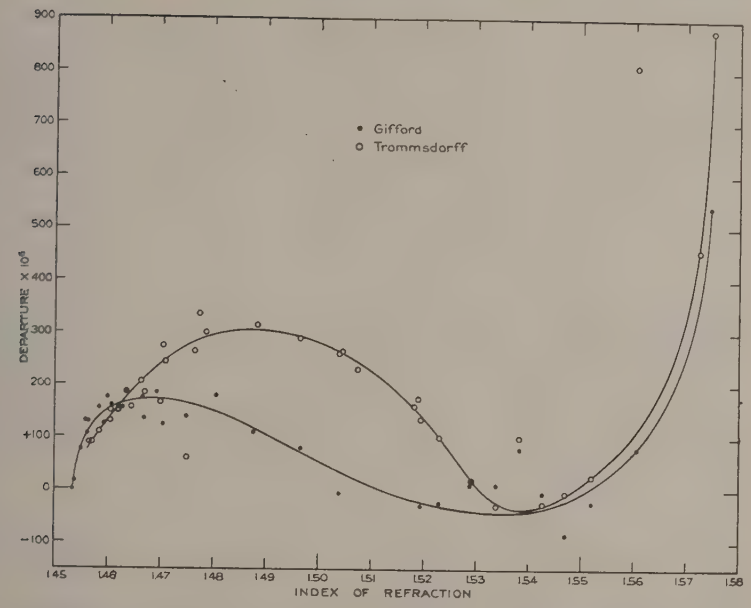


FIG. XXX.6.—Departures of the index of refraction of vitreous silica, as experimentally measured, from a theoretical smooth curve of reference.

TABLE XXX.6.

INDICES OF REFRACTION OF VITREOUS SILICA. RIEDEL, 1903; RINNE, 1914; WATSON, 1890.

Radiation	Wave-length mμ	*N*, Riedel	*N*, Rinne (18°)	*N*, Watson
Rb	420.181			1.468 1
Solar G	430.79	1.466 97		
Violet	440.		1.466 4	
Sr	460.734			1.464 7
He blue	471.315		1.464 5	
Solar F	486.133	1.463 22		
He	501.568		1.462 5	
Tl	535.047			1.460 8
He	587.563		1.458 8	
Solar D (Na)	589.29	1.458 48		1.458 7
Solar C	656.278	1.456 45		
He	667.815		1.456 5	
Li	670.786			1.456 0
He	735.		1.455 1	
Solar A	760.7	1.453 97		

Evaluation of the data

The set of most probable indices for the range 185 to 795 mμ adopted in Table XXX.2 have been derived from the data of Gifford and of Trommsdorff. The data were evaluated by Merwin's method of interpolation.[14] For each wave-length a theoretical index n_λ was calculated by means of the formula

$$N_\lambda = N_{Rb} + (M_{\lambda-0.4} - M_{794.5})\left(\frac{N_{Al} - N_{Rb}}{M_{193.123} - M_{794.5}}\right)$$

in which N_{Rb} and N_{Al} are Gifford's indices for vitreous silica for wave-lengths 794.763 and 193.58 mμ, respectively, and $M_{794.5}$, etc., are values from Merwin's table[15] for the wave-lengths indicated by the subscripts. The final factor is constant and has the value 0.29923.

This calculation gives a smooth curve similar in form to that for N^ω of quartz. It only remains, then, to calculate the amounts by which the actually measured indices of Gifford and of Trommsdorff depart from this curve. The departures are plotted in Figure XXX.6, against the index as abscissa.

The two series practically coincide for wave-lengths below 210 and above 500 mμ, but in the range between these two wave-lengths the difference is real, and probably represents some kind of a difference between the two specimens, although it is just possible that it is due to a concealed error in one or the other series. The data in Table XXX.2 represent an intermediate curve running somewhat nearer to Gifford's than to Trommsdorff's, as Gifford's seem the more reliable (see p. 626).

The experimental data on the indices of low-cristobalite

Since no one has ever had a homogeneous crystal of low-cristobalite, measurements of its indices have necessarily failed to attain high accuracy. It is difficult even to disentangle the three indices (p. 586), because of the finely twinned character of the material (see pp. 131, 200). The mean index can be determined by the familiar method of immersion, under the microscope, in liquids of known index, but to determine n_α, n_β, and n_γ separately requires the study of individual crystals of known orientation.

All the measurements have been made in sodium light, or in white light with liquids calibrated for sodium light. Fenner[16] has made the only estimate of the individual indices, and gives, for 24°C, $n_\alpha = 1.484$ and $n_\gamma = 1.487$,

[14] Merwin, H. E., Amer. J. Sci. (1917) **43**: 49-56. I am indebted to Dr. Merwin for making the calculations and preparing the data on vitreous silica for Figure XXX.6.

[15] p. 51 of article cited.

[16] p. 354 of article cited in IV, note [2].

n_β being intermediate but unknown. Wright[17] gives for n_γ the two values 1.483 ± 0.003 and 1.485 ± 0.003.

Determinations of the mean index are assembled in Table XXX.7. All of these seem to have been made by the immersion method except Mallard's, which was done with a small prism.

TABLE XXX.7.

EXPERIMENTAL DETERMINATIONS OF THE AVERAGE INDEX OF REFRACTION OF LOW-CRISTOBALITE AT ROOM TEMPERATURE.

Observer	n	Source of cristobalite	Reference
Mallard	1.482	Natural, from San Cristobal	Bull. Soc. Min. (1890) **13**: 161.
Rieke & Endell.....	1.48 to 1.49	From chalcedony	Z. anorg. Chem. (1912) **79**: 239.
Rieke & Endell.....	1.485	Vitreous silica at 1450°	Tscherm. Mitt. (1912) **31**: 501.
Bowen & Andersen....	1.485 ± 0.001	Melts in system SiO_2—MgO	Am. J. Sci. (1914) **37**: 487.
Ramdohr	1.485	Devitrification soft glass	Centr. Min. 1920: 33.
Washburn & Navias...	1.484	Flint and Na_2WO_4 at 1500°	J. Am. Ceram. S. (1922) **5**: 584.
Washburn & Navias...	1.483	Flint at 1430 to 1460°	
Washburn & Navias...	1.456 to 1.470	Chalcedony at 1430 to 1460°	

THE DATA ON THE REFRACTIVE INDICES OF LOW-TRIDYMITE

Low-tridymite offers the same difficulties as low-cristobalite in the measurement of its indices, for it, too, becomes twinned by the inversions, and homogeneous crystal fragments of large size are not available at room temperature.

Measurements of the individual indices and of the average index are compared in Table XXX.8. All the data are for sodium light. Most of the determinations were made by the immersion method. Mallard's were made on a natural prism. Lasaulx's are abnormally low, but were done by a method (that of the Duc de Chaulnes) which is not as reliable as those usually employed.

THE REFRACTION OF X-RAYS

The general tables given in the first part of this chapter cover the visible and the nearer ultra-violet and ultra-red frequencies. But even waves so short as the X-rays are subject to true refraction and reflection, and should also be considered here. This effect is very different from that described in Chapter XIII, which depends upon diffraction, due to scattering and interference. We are concerned now with retardation of speed, which leads to refraction and reflection of a ray.

[17] DAY, SHEPHERD, & WRIGHT, article cited in V, note [3].

Because of the very high frequency, the angles are very small and difficult of measurement. The index of refraction differs from 1 by only about 0.000 002.

No measurements have been attempted on pure silica, but Compton [18] has shown that X-rays can be totally reflected in passing from air into glass, at an angle of about 6 minutes. The refractive index of the glass in air, for X-rays, is therefore *less* than 1, and total reflection occurs when the rays pass from the lighter into the denser medium, just the opposite of the usual conditions for total reflection (see p. 698).

TABLE XXX.8.

EXPERIMENTAL DATA ON THE REFRACTIVE INDICES OF LOW-TRIDYMITE.

A. INDIVIDUAL INDICES.

Observer	n_α	n_β	n_γ	Source	Reference
Lasaulx	1.4107	1.4285	....	Natural	Z. Kryst. (1878) **2**: 272.
Mallard	1.4773	1.4775	1.4791	Natural (Mexico; France)	Bull. Soc. Fr. Min. (1890) **13**: 169.
Fenner	1.469	1.469	1.473	Quartz in tungstate melt	Am. J. Sci. (1913) **36**: 351.
Schaller	1.472	....	1.477	Rhyolite, Nevada	U. S. Geol. Surv. Bull. 640 G (1916).
Wilson	1.473	....	1.474	Devitrif. glass	J. Soc. Gl. Tech. (1918) **2**: 186.
Merwin	....	....	1.474	From quartz at 1350°	Am. J. Sci. (1918) **46**: 425.
Merwin	....	....	1.474	Glass-furnace brick	
Merwin	....	....	1.474	Cerro San Cristobal	
Merwin	....	....	1.474	Colorado(?)	

B. AVERAGE INDEX, OR INDEX UNDEFINED BY AUTHOR.

Observer	n	Source	Reference
Clews & Thompson.....	1.478	Quartz in melted NaCl	J. Chem. Soc. (1922) **121**: 1442.
Washburn & Navias....	1.475	Flint in Na_2WO_4 at 1300°	J. Am. Ceram. Soc. (1922) **5**: 584.

Theory

The index of refraction of a substance for X-rays should be less than 1, even in vacuum, if the electrons mainly responsible for causing dispersion have a frequency less than that of the radiation. The experiment just referred to shows that such is the case in a silicate glass, but in so complex a material it is impossible to say which of the various electrons are concerned in the refraction. Experiments on pure vitreous silica might reveal some information about the movement of electrons in SiO_2, and in particular, experiments near an inversion-point might furnish

[18] See DOAN, R. L., Phys. Rev. (1926) **27**: 796.

evidence for or against the electron theory of the inversions of silica presented in Chapter XV.

Comparative results on a natural glass surface and on natural and artificial vitreous silica surfaces might conceivably supply information concerning the orientation of molecules in a natural surface of molten glass (see p. 514).

Indices of refraction of the micro-forms

Chalcedonic silica

The unsatisfactory state of the classification of the micro-crystalline fibrous varieties of silica usually included under the general name of "chalcedony" has already been commented upon (Chap. X), and a few details of optical properties were given in connection with some proposed classifications.

The only general statement that can be made concerning the index of refraction is that its average value for chalcedonic silica, as is to be expected from the constitution of the material (p. 272) is lower than the low index n_ω of quartz (1.544 for sodium light). 1.54 may be taken as an approximate maximum. Increase in the amount of micro-amorphous silica or of water in the interfibrous opaline silica lowers the index below this value. This holds, of course, for material in which the fibers are sub-microscopic, so that only an average index is measurable.

Some typical measurements are assembled in Table XXX.9. A value often quoted is that of Des Cloiseaux,[19] 1.537 in red light.

Although only a single index is given here, the material nearly always appears birefringent (see p. 585). There is difference of opinion as to whether it is uniaxial or biaxial. The birefringence is small, of the order of 0.009 to 0.011, about the same as that of quartz.

Table XXX.9.

Experimental Data on the Average Refractive Index of Chalcedonic Silica.

Observer	N_{Na}	Material	Reference
Robson	1.540	Chalcedony, S.W. Illinois	J. Am. Ceram. Soc. (1922) **5**: 670.
Washburn & Navias...	1.533 to 1.538	Chalcedony, Yellowstone Park	J. Am. Ceram. Soc. (1922) **5**: 565.
Washburn & Navias...	1.533 to 1.539	"French flint"	J. Am. Ceram. Soc. (1922) **5**: 565.
Robson	1.527	"French flint" calcined and pulverized	Cited above.

[19] Minéralogie (1862) Vol. 1, p. 20.

Individual indices of the variety of silica known as quartzine have been determined for 3 solar frequencies by Wallerant.[20] The data are:

Radiation Solar line	N_α	N_β	N_γ
C	1.531	1.534	1.540
D	1.5325	1.5355	1.5435
F	1.537	1.540	1.548

Micro-cristobalite

The apparent index of refraction of micro-crystalline cristobalite produced by the action of high temperatures on a micro-crystalline or finely fibrous variety of silica may be notably lower than that given in Table XXX.1. This low index accompanies the low apparent density of such cristobalite.

This apparently low index is in fact not the index of the crystalline particles, but is the average index of an aggregate made up of crystals and air-spaces or vacuum-spaces, too small to be visible under the microscope.

This is the reason why fine-grained cristobalite produced at high temperatures has sometimes been mistaken for isotropic amorphous or vitreous silica, as, for instance, by Le Chatelier (1890), Herschkowitsch (1903), Holmquist (1911), and Endell (1912).

Washburn & Navias[21] found that the index of cristobalite made by heating chalcedony (from Yellowstone Park) was 1.456 to 1.470, thus ranging from 0.015 to 0.029 less than the true average index of crystalline cristobalite. Cristobalite made by heating black French flint had an index of 1.483, only 0.002 low.

Micro-amorphous silica

The index of micro-amorphous silica is sensibly the same as that of vitreous silica, 1.459 for sodium light. Typical observations are:

Observer	N_{Na}	Material
Wright	1.459 ± 0.003	Precipitated from solution
Wartenberg[22]	1.46	Made by reduction and reoxidation

[20] WALLERANT, F., *Mémoire sur la quartzine et sur l'origine de la polarisation rotatoire du quartz*, Bull. Soc. Franc. Mineral. (1897) **20**: 52-100, pls. 1-4.

[21] Proc. Natl. Acad. Sci. (1922) **8**: 1-5.

[22] Article cited in VI, note [68].

Chapter XXXI. THE REFRACTIVE INDICES OF QUARTZ

The most probable values of N_ϵ and N_ω for quartz at 18° have been tabulated and represented graphically in Chapter XXX (Tab. XXX.2, Fig. XXX.1). The present chapter will give the original data and the evidence concerning the degree of constancy of the indices.

The experimental data on the refractive indices of quartz

A great many measurements have been made on the refractivity of quartz. The data at room temperatures may be grouped for purposes of discussion into the following classes:

(a) Measurements of high precision, designed to compare the refractivity of quartz from different sources. Some of these measurements are at a single frequency, others at several frequencies. They furnish an answer to the important question as to the constancy of the property.

(b) Miscellaneous single measurements, some of high accuracy, some of low accuracy, usually at only a single frequency.

(c) Measurements of high accuracy and precision, taking account of temperature and sources of small errors, and designed to show the relation of refractivity to frequency.

(d) Measurements designed to show the relation of refractivity to frequency, but not of the highest contemporary accuracy.

In view of the existence of several good series of measurements of classes (a) and (c), data of class (d) and data of low accuracy in class (b) do not have much value for our present purpose. Nevertheless it is desirable that they should be assembled and examined with an eye for anomalous specimens, whose further study might throw light on possible variations in the structure, inversion-temperature, or other properties.

Effect of temperature and other variables

For obvious practical reasons, the indices are nearly always measured in air, and the specimen and surrounding air are at the same temperature. The result, then, is the index of refraction at temperature t referred to air at temperature t and pressure p. As the index of air itself changes with t and p, such results need to be reduced to some standard state. The usual custom is to give the index of the substance at temperature t, in air at 15° and 760 mm pressure.

Not all authors have been careful to specify the conditions of measurement, and the real meaning of the published result is sometimes in doubt. In the absence of specific statement, it must be assumed that the results are indices in air at the same temperature as the specimen.

The variations due to the atmospheric variables, including even changes

in the amounts of water vapor and carbon dioxide in the air, are easily measurable in exact work, though not noticeable in ordinary work. Examples of the effects to be expected on some assumed indices near those of quartz are shown below:

	$\lambda = 200$ mμ	$\lambda = 589$ mμ	$\lambda = 1000$ mμ
Assumed absolute index (in vacuum)..	1.650 000	1.545 000	1.535 000
Change in absolute index caused by rise of 1° C in temp. of quartz.....	+ 0.000 001	— 0.000 006	
Same index referred to air at 15° and 760 mm	1.649 463	1.544 573	1.534 580
Same index referred to air at 20° and 760 mm	1.649 473	1.544 580	1.534 587
Apparent change of index caused by rise of 10 mm in p.....	— 0.000 007	— 0.000 006	— 0.000 006

Experimental data on the constancy of the indices of quartz

The simple comparison of indices as determined by various observers is hardly sufficient evidence for or against the existence of differences in the index among different specimens of quartz. The indices of clear unexceptionable crystals are so nearly the same that apparent differences may fall within the limits of accidental or concealed errors. To obtain reliable evidence on the constancy of the indices of quartz it is necessary that the same observer shall compare the specimens under comparable conditions and with the same apparatus.

We shall consider first the comparisons of this kind which have yielded positive and accurate evidence on the question. Such have been made by Gifford (1902), Macé de Lépinay & Buisson (1904), and Buisson (1906).

Gifford[1] made an accurate comparison of the indices of right-quartz and left-quartz, using two large prisms of the same size, and determining also their relative density. The results, which are indices at 15° in air at 15° for wave-length 589.317 mμ, are as follows:

Specimen	N_ϵ	N_ω	"Sp. grav."
Right-quartz, first det.....	1.553 366 2	1.544 255 8	2.6495
Right-quartz, second det.....	1.553 367 3	1.544 255 8	
Left-quartz	1.553 345 2	1.544 236 3	2.6511
Right—Left	0.000 021 6	0.000 019 5	— 0.0016

The difference in index is in the fifth place, and the right-handed crystal is the higher.

A further important point is that the difference in index is opposite in sign to the difference in density. This is the reverse of what was to have been

[1] Gifford, J. W., *The refractive indices of fluorite, quartz, and calcite,* Proc. Roy. Soc. London (1902) **70**: 329-340.

expected, since density and refractivity are properties which usually change in the same direction.

A set of measurements made by Buisson [2] on very large specimens, and by an optical interference method, yielded a set of results of very high precision, namely 0.3×10^{-6}, although the absolute accuracy is of no such degree.

These measurements showed definitely a difference in refractive index not only between different specimens of quartz but between different parts of the same specimen. The results are brought together in Table XXXI.1. The two cubes of quartz are the two which were used by Macé de Lépinay and others in the work on the density of water, already referred to in Chapter XVIII.

TABLE XXXI.1.

DIFFERENCES IN THE INDEX OF REFRACTION OF QUARTZ. BUISSON, 1906.

$t = 11°C$. Absolute index.

	n_ϵ		n_ω	
	Cd red	Cd green	Cd red	Cd green
a. 4-cm cube	1.551 790 5	1.557 941 1	1.542 739 1	1.548 687 6
b. 5-cm cube, one part	1.551 776 6	1.557 926 5	1.542 728 6	1.548 676 9
c. 5-cm cube, another part 5 cm distant from the first	1.551 784 4	1.557 935 0	1.542 733 5	1.548 682 1
(a—b) $\times 10^6$.....	13.9	14.6	10.5	10.7
(c—b) $\times 10^6$.....	7.8	8.5	4.9	5.2

Macé de Lépinay & Buisson [3] also observed a difference of about 6×10^{-6} between two portions, 5 cm apart, of a 20-mm plate cut from the same crystal as the 5-cm cube. Another plate, 10 mm thick, and a 36-mm prism, both likewise cut from this same crystal, agreed in index with the portion of higher index in the 20-mm plate, within the limits of error of each comparison (0.6 to 2.0×10^{-6}).

All of these specimens, however, had a slightly higher index (0.5 to 6×10^{-6}) than another large prism "PW," and the same authors report that still another specimen of quartz, used in 1902, showed differences in refractive index of about 6.0×10^{-6} from "PW."

The data as a whole, then, give good evidence of possible differences in index between these specimens, amounting to about 10×10^{-6}. It is true that Schönrock [4] has mildly criticized the comparisons by Buisson, pointing out that sufficient proof of planeness of faces and exactness of orientation is not presented in the paper, and that the Nörrenberg polarization apparatus used is not very sensitive to optical anomalies, so that the 5-cm cube C_ϵ may not have been as optically clear as supposed. But he agrees with Buisson that differences of this magnitude do exist between specimens of quartz.

[2] BUISSON, H., article cited in XX, note [4].

[3] MACÉ DE LÉPINAY, J., & BUISSON, H., *Sur une nouvelle méthode de mesure des épaisseurs et des indices* . . . . Ann. Chim. et Phys. (1904) (8) **2**: 78-108.

[4] Zeitschr. Instrument. (1907) **27**: 24-25.

It is worth noting from the data in Table XXXI.1 (Buisson) that the birefringence, $N_\epsilon - N_\omega$, varies in the same direction as the index of refraction. The dispersion (N green $- N$ red), however, is constant for both indices. This constancy was also noted by Macé de Lépinay & Buisson in the measurements just referred to.

Macé de Lépinay [5] compared indirectly the indices of two specimens of quartz with those of a third specimen (his 4-cm cube) whose indices had been determined independently. The comparison was made through comparing the thickness of the plates as determined by their birefringence, a method which assumes the indices to be the same as in the standard cube, with the thickness of the plates as determined by the use of Talbot's fringes. The results are:

Plate	L.2	W'20
Thickness by birefringence, mm.....	2.008 41	19.960 35
Thickness by Talbot fringes, mm.....	2.008 66	19.960 54

These figures indicate a difference in index between L.2 and the standard cube of about 190×10^{-6}, and between W' 20 and the cube of about 15×10^{-6}.

We have positive evidence, then, that the indices of refraction of any random specimen of clear quartz of optical grade may differ by at least 20×10^{-6} or 0.000 02 from the indices of any other random specimen. This may be considered the lower limit of constancy, beyond which we may not expect to go without setting up some definite quantitative specifications for the quality of the specimen.

The next question concerns the upper limit. How large a variation is it possible to find in quartz which is optically acceptable? A simple inspection of the data listed in various parts of this chapter, allowing for experimental error, indicates that the indices of all kinds of clear quartz specimens are constant to at least 500×10^{-6} or 0.000 5. How much better are they than this limit?

Evidence on this question has been offered by Schrauf (1860), Fizeau (1864), Van der Willigen (1870), Quincke (1877), Kohlrausch (1877), Sorby (1878), Hallock (1881), Danker (1886), Dufet (1890), Hlawatsch (1897), Merwin (1911), and Pérard (1922).

Summarizing the results which follow, we may say that the difference between two extreme specimens of clear optically acceptable quartz may possibly reach 200×10^{-6}, but if it exceeds this value either the apparatus or the method is subject to suspicion.

Schrauf [6] made a series of measurements on small but perfectly formed quartz crystals from St. Gotthard, using the natural hexagonal prism. Measurements were made with sunlight, at 5 frequencies and on 4 prisms. The precision was about 150×10^{-6}. The differences between specimens are in

[5] Macé de Lépinay, J., *Détermination des constantes optiques du quartz . . .*, Journ. de Physique (1900) (3) **9**: 644-652.

[6] Schrauf, A., Sitzungsb. Akad. Wiss. Wien (1860) **42**: 107-145.

some cases greater than this, but are probably due to errors in the prism angles or to lack of planeness in the faces, since the angles and faces were natural.

Fizeau[7] used one cube of right-quartz and one of left-quartz in his measurements of the dilatation of quartz, and two right- and two left-quartz plates in his accompanying observations on the movement of interference bands as a result of rising temperature, an effect due to the simultaneous effects of dilatation and change of refractive index. No systematic differences could be detected between the right and left specimens.

At the same time the indices of refraction at room temperature were determined on two 60-degree prisms cut from two of the plates, with the following results:

	Rotation	t	N_ϵ	N_ω
Prism 11	Left	16.4	1.553 61	1.544 46
Prism 12	Right	17.8	1.553 65	1.544 36
Diff. (11—12)			-40×10^{-6}	$+100 \times 10^{-6}$

Van der Willigen's series of measurements (see p. 622) covered 3 specimens, but the precision on the first was too low to permit its inclusion in a comparison of this kind. The results on numbers II and III, as compared by the author himself, are shown in Table XXXI.2. He uses the means of the values at 19 frequencies, and calculates the differences to be expected from his own determinations of the temperature coefficients of the indices.

TABLE XXXI.2.

COMPARISON OF THE INDICES OF TWO SPECIMENS OF QUARTZ. VAN DER WILLIGEN.

Mean of 19 frequencies.

	Specimen II	Specimen III	Difference II—III	
			Obs.	Calc.
Rotation	Left	Right		
Mean of the 19 values of N_ω	1.548 770	1.548 720	$+50 \times 10^{-6}$	-44×10^{-6}
Average temperature	23.6°	16.0°	7.6°	
Mean of the 19 values of N_ϵ	1.558 013	1.557 954	$+59 \times 10^{-6}$	-54×10^{-6}
Average temperature	23.8°	16.8°	7.0°	

It is evident from the Table that the difference is opposite in sign to that expected from the difference between the temperatures at which the two series happen to have been made. As the precision is apparently of the order of 5×10^{-6}, the amount of the difference is also well outside of the experimental error. It comes to about 1 in the fourth decimal place, the left-rotating crystal being the higher.

Pérard,[8] in determining the indices of the quartz employed for length

[7] FIZEAU, H., article cited in XX, note [13].
[8] p. 260 of article cited in note [34].

standards at the International Bureau, noted that the indices differed by very little more than the possible errors of observation. From the data given I judge this to mean agreement within about 10×10^{-6}. The various standards were probably cut from quartz from the same source.

The most extended series of comparisons between different kinds of quartz is that of Dufet.[9] He compared 20 specimens, most of which, however, were colored, with a standard crystal (the one used by Benoit for dilatation measurements; see p. 378). The comparisons were made on an Abbe-Pulfrich refractometer, each measurement being preceded and followed by settings on the standard, so that the highest differential precision could be obtained. The precision on a single setting was about 10×10^{-6}; hence a difference of 2 or 3 in the sixth place is equivalent to identity within the limits of the method.

The results on several optical plates, probably of Brazilian quartz, were:

No.	Description	Difference from standard quartz, in ordinary index N_ω, for D line
1.	Clear, cut parallel to axis	$+ 3 \times 10^{-6}$
2.	Clear, cut perpendicular to axis, right-handed	$+ 3 \times 10^{-6}$
3.	Clear, cut perpendicular to axis, "à deux rotations"	$- 3 \times 10^{-6}$
4.	Clear, cut oblique to axis	$- 1 \times 10^{-6}$

These specimens are thus practically identical in index with the standard, but since they are probably all from the same source and possibly even from the same crystal or batch of crystals, this degree of agreement might naturally have been expected. The comparison with the colored crystals will be taken up at a later page.

Merwin[10] compared the indices of refraction in sodium light of several of the specimens of quartz which he used in testing the constancy of their density (see p. 297). 5 specimens were carefully measured on an Abbe-Pulfrich refractometer, whose hemisphere and scales were calibrated by observations of the angle of total reflection from air, water, and standardized specimens of crown glass, flint glass, and a lime-magnesia-silica glass. The 5 quartz specimens included those of highest and lowest density in the density series.

Small differences were found, paralleling the differences in density, the densest quartz having the highest index and the lightest quartz the lowest index. The differences were just about on the limit of sensitivity, however, namely about 50×10^{-6}. The total range was about 150×10^{-6}. The quartz of maximum density and index was also measured on a spectrometer. The results are:

	N_ω	
Quartz from Herkimer County, New York	1.544 28	(spectrometer)
Quartz from Herkimer County, New York	1.544 3–	(refractometer)
Quartz from Brazil (pebble)	1.544 3–	(refractometer)
3 specimens, source unknown	1.544 2	(refractometer)

[9] DUFET, H., *Mesures comparatives de l'indice de differents quartz*, Bull. Soc. Franc. Mineral. (1890) **13**: 271-276.

[10] MERWIN, H. E., article cited in XVIII, note [19].

The range of differences indicated is thus of a larger order of magnitude than that of Dufet's optical specimens, and is about the same as found by Dufet for his colored quartzes (see Tab. XXXI.3).

TABLE XXXI.3.

DIFFERENCES IN ORDINARY REFRACTIVE INDEX N_ω, FOR D LINE, OF SPECIMENS OF COLORED QUARTZ AS COMPARED WITH A STANDARD OPTICAL QUARTZ. DUFET, 1890.

No.	Source	Description	Form or direction	Difference $\times 10^6$
5	Saint-Etienne-du Bois, Vendée(?), France	Clear, slightly yellowish	Rounded fragments	+ 2
6	Saint-Gothard	Very dark smoky. Right-rotating	Cut perpendicular to axis	+ 9
7	Unknown	Dark smoky	Cut parallel to axis First area Second area	 — 74 — 14
8	Champ-Bretault, Orne, France	Smoky	Cut parallel to axis First area Second area	 — 69 0
9	Unknown	Yellow (false topaz)		— 6
10	Unknown	Rose, slightly milky		— 22
11	United States	Dark amethyst, tint homogeneous	Cut oblique to axis	+ 44
12		Amethyst, with optic anomalies and bands superposed in ternary symmetry		+ 49
13		Amethyst, pale, homogeneous		+ 61
14		Amethyst, pale, mixed with milky quartz of oily luster (gras)		+ 49
15	Tammela, Finland	Rose		+ 65
16	Westfalen, Germany	Milky, bipyramidal	Cut parallel to axis First area Second area	 — 21 — 113
17		Smoky, formed of small grouped crystals		+ 98

Kozu[11] measured both of the indices of quartz on a plate perpendicular to the axis, with a refractometer whose hemisphere had been previously calibrated by comparison with a glass prism. The index of the prism was accurately determined with a Fuess goniometer. In the measurements on quartz 6 frequencies were used, selected from the arc or Nernst light by means of a Hilger spectrometer. The results agree with those of Gifford (p. 617) within, at most, 50×10^{-6}, which is about the limit of accuracy of the method, and no drift of

[11] Kozu, S., Mineral. Mag. (1916) **7**: 253-273.

the differences is noticeable. All the differences but one, however, are positive; that is, Kozu's indices tend to be higher than Gifford's. This may represent a constant error which is just on the limit of accuracy, or it may represent a real difference between the specimens, of the order of 50×10^{-6}.

The indices obtained by Rudberg[12] from his prism No. 2 are 40 to 100×10^{-6} higher than those from No. 1, but the author ascribes the difference to experimental error. A constant error in the angles may possibly account for it, and in view of the author's disclaimer we are not justified in concluding that there was any real difference between the two specimens.

Colored quartz

Quartz containing sufficient impurities to give it a noticeable color might reasonably be expected to differ in refractive index from clear colorless quartz, if the coloring matter be in units of the size of a wavelength of light or smaller. If larger than this, they should not affect the index although they might make it difficult to determine with precision, because of the scattering of light.

Dufet's comparisons, already referred to, are the most extensive. His results on colored specimens are given in Table XXXI.3.

Inspection of the table shows that the amethysts and one rose quartz have a higher index than the standard, while the smoky quartzes are generally lower. As shown in three instances, different areas in a given specimen of smoky quartz may differ considerably in index, as also in color, the smokiness being irregularly distributed in many such specimens.

The last three values are on less transparent specimens and are therefore less precise.

Hlawatsch[13] followed up this work of Dufet by comparing 3 specimens of quartz from St. Gotthard, one clear, the others smoky gray, using the prism method instead of total reflection. The results were:

	N_ϵ	N_ω
Colorless quartz	1.553 05	1.544 33
Smoky gray, first specimen	1.553 17	1.543 88
Smoky gray, second specimen		
Light colored portion	1.552 99	1.544 03
Dark colored portion	1.552 89	1.543 87
Latter after heating	1.553 44	1.544 36

The apparently low value of N_ϵ for the colorless crystal is ascribed to a slightly tapering specimen.

In general the results agree with Dufet's in that smoky quartz has a lower index than colorless quartz.

The last pair of measurements shows that the lowered index is really asso-

[12] Article cited in note [44]

[13] Hlawatsch, C., *Ueber den Brechungsexponenten einiger pigmentirter Mineralien*, Zeitschr. Krystall. (1897) **27**: 605-607.

ciated with the color. The darker part of the crystal was heated at "somewhat below a bright red" temperature for 3 hours, which rendered it colorless and at the same time raised its index to equality with that of the colorless quartz.

A similar lowering of index by a "smoky" coloring matter was also observed by Hlawatsch in sillimanite and fluorite.

Kohlrausch [14] compared the indices of colorless quartz with those of amethyst and citrine-quartz, in the course of a series of measurements to test out his newly devised method for the measurement of indices by total reflection in carbon bisulfide. The results for sodium light (line D) are:

	t	N_ϵ	N_ω
Quartz, plate ⊥ axis	23	1.5530	1.5438
Quartz, plate ∥ axis	24	1.5531	1.5436
Amethyst	23	1.5533	1.5440
Citrine-quartz, surface ∥	22	1.5532	1.5444
Same, with axis horizontal	22	....	1.5445

Hallock [15] made a series of measurements on 13 quartz plates, and on the pyramid and prism faces of one specimen, a total of 27 surfaces, at temperatures of 19.5 to 26°. The highest and lowest indices obtained were:

	N_ϵ	N_ω
Maximum	1.5527	1.5433
Minimum	1.5519	1.5426
Difference	0.0008	0.0007

The precision of the individual measurements was about 0.0002, but the indices given above were calculated from measurements made with reference to carbon bisulfide, which, as the author notes, has a relatively large temperature coefficient (0.0008 per degree). The net accuracy is therefore probably of about the order of magnitude of the difference between the maximum and minimum quoted above. The effect of the variable temperature on the indices of the quartz itself could have been, at the maximum, 0.000 04, and so would not enter into the comparison.

The net result, therefore, is that the indices of these quartzes are constant within 0.000 5, between 14 different specimens.

Using his newly invented method of measuring the index of refraction of a mineral on the microscope stage through the amount of refocussing made necessary by its introduction, Sorby [16] noted that there was a "slight but well-marked difference in the index for different specimens" of quartz. The method is not, however, very precise,—about 0.001 to 0.002,—and the value at index 1.5 is subject to a negative correction of 0.010 because of the spherical aberration due to the introduction of the mineral section or plate. It seems likely, therefore, that the differences observed by Sorby may be ascribed wholly to the method and not to the specimens.

[14] Kohlrausch, F., Verhandl. physikal.-med. Ges. Würzburg (1877) **12**: 103-110.
[15] Hallock, W., *Ueber die Lichtgeschwindigkeit in verschiedenen Quarzflächen*, Ann. Physik u. Chem. (1881) **12**: 147-149.
[16] Sorby, H. C., Mineral. Mag. (1878) **2**: 103-105.

Quincke[17] measured the indices of 3 quartz plates by a total reflection method, the plate being held between two flint glass prisms, with films of oil between the surfaces. 7 frequencies (solar lines A to G) were employed. The differences between the specimens, which were in the fourth and even in the third decimal place, were attributed by Quincke to the quartz itself, but this proved to be an error, as we shall see in the next few paragraphs.

Supposed surface effects

A problem which arose in the course of the comparisons described in preceding paragraphs was that of the possible difference in refractivity between the interior of a crystal and its polished surface, and also the effect of changes in the surface due to age or to the adsorption of moisture or other substances.

Quincke[18] reported in 1879 that the index of refraction measured by the total reflection method on the faces of some old specimens of quartz, some of which had been in his possession for 20 years, were not only very divergent but fell considerably below the values for freshly polished surfaces. The indices, for the D line, observed on the old plates varied from 1.5141 to 1.5374 for N_ω and from 1.5216 to 1.5470 for N_ϵ.

These differences are very large, and they naturally aroused some astonishment and incredulity. They led Hallock[19] to make the series of comparisons already referred to, and also to make the following experiment. One of his older plates, 4b (supposed to be about 10 years old) was reground and repolished, with the following results:

	t	N_ϵ	N_ω
Original	19.7	1.5522	1.5427
Reground	25.4	1.5526	1.5434
Repolished	21.7	1.5521	1.5427

The indices were found constant within the limits of possible error, which were not extremely small, to be sure, yet were of a smaller order of magnitude than Quincke's differences.

It appears, therefore, that there must have been some unrecognized source of error in Quincke's measurements, possibly a lack of parallelism between the faces of the adhering prisms and the faces of the plate, or even between the two faces of some of the plates.

Danker[20] made a series of measurements on uniaxial and biaxial substances with the purpose of testing the conclusions as to total reflection which are deducible from the general principles of birefringency. These measurements yielded the following data for quartz from Middleville, Herkimer County, New York; frequency, line D:

[17] Quincke, G., Festschr. Naturforsch. Ges. Halle **1879**: 321-328.
[18] Article just cited.
[19] Article cited in note [15].
[20] Danker, J., Neues Jahrb. Mineral. etc. (1886) Beilage-Bd. **4**: 241-290, especially pp. 266-269.

	t	N_ϵ	N_ω
Natural prism face	22	1.553 52	1.544 42
Polished prism face	19.5	1.553 51	1.544 42

The following comparisons were also made on a quartz prism, in order to discover, if possible, any effect of the surface:

Method	t	N_ϵ	N_ω
Minimum deviation	20	1.553 10	1.543 97
Grazing incidence	19.5	1.553 18	1.544 07
Total reflection	18.5	1.553 22	1.544 25

The differences are stated by the author to be within the limits of error of observation, and so indicate no difference of more than 0.000 3 between the interior and the polished surface.

Dufet[2] made a direct comparison between the minimum-deviation and the total-reflection methods of determining the index. The minimum-deviation method on an equilateral prism of quartz, read on all three angles, gave for the D line at 18°C: $N_\omega = 1.544\ 240 \pm 0.000\ 007$. Using this value for quartz as a basis, together with his previously determined temperature-coefficient for quartz (see p. 676) Dufet obtained the index of the hemisphere of his Abbe-Pulfrich refractometer, and also measured that index directly on a prism of the same glass, obtaining these values at 15°:

Index based on quartz	1.614 475
Index directly measured	1.614 474

It follows that the index obtained for quartz by the total-reflection method with the Abbe-Pulfrich refractometer is identical with that measured on the quartz prism, within the sensitiveness of the measurements.

Similar tests with other substances, using quartz as a standard of comparison, showed that in soft substances surface film effects due to polishing may cause the index obtained on the refractometer to be larger, by various amounts up to 20×10^{-4}, than the index determined on a prism. These differences are much smaller than would be expected from the large effects which surface polishing produces in the angle of polarization by reflection.

As the matter stands now, therefore, we can be fairly sure that the index of refraction of quartz as obtained by total reflection at a surface is in agreement with that obtained by the deviation of a ray, to within 5×10^{-6} and probably better.

Miscellaneous measurements at a single frequency or on a single specimen of quartz

We may dismiss at once measurements made with immersion liquids under the petrographic microscope. For some substances this is the only

[2] Dufet, H., Bull. Soc. Franc. Mineral. (1891) **14**: 130-148.

method available, as when the material is obtainable only in fine powder or microscopic crystals, and it is also quite accurate enough for most purposes, because most substances are not so reproducible that the index will not vary in the fourth or even third decimal place. But the method is not to be considered a source of data of any consequence for a substance like quartz, which is obtainable in a fairly pure state and in large and perfect crystals.

TABLE XXXI.4.

MACÉ DE LÉPINAY'S MEASUREMENTS OF THE ORDINARY INDEX OF REFRACTION n_ω OF QUARTZ FOR CADMIUM GREEN LIGHT ($\lambda = 508.7237$ mμ IN VACUUM).

Formula: $n_\omega = 1.548\,738\,1 - 10^{-9}\,(5168\,t + 15.52\,t^2)$.

t	Index observed	Deviation from formula. Deviation × 10^6
	Group (1). A_1, B_2, C_3.	
7.60	1.548 697 6	−0.3
16.14	1.548 651 0	+0.3
26.04	1.548 592 2	−0.8
	Group (2). A_2, B_3, C_1.	
8.21	1.548 694 5	−0.2
16.80	1.548 646 2	−0.7
26.43	1.548 590 4	−0.3
	Group (3). A_3, B_1, C_2.	
7.90	1.548 696 7	+0.4
16.49	1.548 648 8	+0.1
26.40	1.548 591 8	+0.9

The principal methods for the accurate measurement of indices of refraction depend upon: (1) the deviation of a ray passing through a prism of the substance; (2) the retardation of a ray passing through a plate of the substance, resulting in the production of interference fringes when it is combined with an unretarded ray; or (3) the total reflection of a ray at a plane surface of the substance. As usually practiced, the third of these methods is less accurate than either of the other two.

One of the most precise measurements ever made of the index of refraction of a given specimen of quartz at a single frequency is that of Macé de Lépinay,[22] made in connection with his research on the relation between the liter and the cubic decimeter (see p. 291). An equilateral triangular prism was used, with faces of a high degree of planeness (minimum radius of curvature 3000 m). Three series were made, at different seasons of the year, in order to obtain the temperature coefficient of the index.

The final means, each resulting from 9 measurements, are given in Table XXXI.4, just to show what can be done in measurements of this kind. The

[22] MACÉ DE LÉPINAY, J., article cited in XVIII, note [23].

values are the ordinary index n_ω for the cadmium green ray of absolute wave-length 508.7237 mμ (508.5823 in air). The letters A, B, C refer to the three angles of the prism, the combination of the three practically eliminating the error in the measurement of a given prism angle since the sum must be 180°. The average deviation from the formula at the head of the table is less than 1 in the sixth place.

The equivalent index at 18°, in air at 18°, is 1.548 215.

Similar measurements were made by Macé de Lépinay[23] in 1895 for the D line, of mean absolute wave-length 589.4603 mμ, but only at temperatures of 19.66 to 22.58° C. They were calculated back to 0° by means of Dufet's formula:

$$n_{\omega o} - n_{\omega t} = 6.22 \times 10^{-6} t + 4.25 \times 10^{-9} t^2$$

The results are:

Angles	n_ω
A_1, B_2, C_3	1.544 776 1
A_2, B_3, C_1	1.544 774 4
A_3, B_1, C_2	1.544 775 9
Mean	1.544 775 5

Notwithstanding the very high precision of the measurements just mentioned, their real accuracy proves to be less than might have been expected. The primary purpose of the measurements was to secure an accurate value of the index for use in the subsequent measurement of the exact dimensions

TABLE XXXI.5.

DETERMINATIONS OF THE REFRACTIVE INDICES OF QUARTZ FOR SODIUM LIGHT (D LINE) IN AIR.

Author	$^\circ\,^t$C	N_ϵ	N_ω
Rudberg (1828)	18	1.553 28	1.544 18
Schrauf (1860)	20	1.553 38	1.544 21
Fizeau (1864)	17	1.553 63	1.544 41
Mascart (1864)	..	1.553 38	1.544 23
Baille (1867)	12	1.553 277	1.544 183
Van der Willigen (1870)	20	1.553 26	1.544 17
Sarasin (1878)	Ab. 15	1.553 35	1.544 19
Soret, C. (1883)	..	1.553 41	1.544 35
Müller (1885)	20	1.553 34	1.544 23
Danker (1886)	20	1.553 42	1.544 33
Mülheims (1888)	..	1.553 28	1.544 23
Dufet (1890)	18	....	1.544 21
Dufet (1891)	18	....	1.544 24
Simon (1894)	Room	....	1.544 16
Macé de Lépinay (1895)	21.0	....	1.544 225
Wülfing (1895)	..	1.553 25	1.544 11
Hlawatsch (1897)	..	....	1.544 33
Reed (1898)	20	1.553 25	1.544 21
Viola (1899)	..	1.553 42	1.544 35
Gifford (1902)	15	1.553 356	1.544 246
Merwin (1911)	Ab. 20	....	1.544 24
Kadokura (1915)	Ab. 20	1.553 215	1.543 950

[23] MACÉ DE LÉPINAY, J., Ann. Chim. et Phys. (1895) (7) **5**: 210-255.

of a 4-cm cube of quartz. Fabry & Perot subsequently developed a method for determining the dimensions independently of the index, and measurements by that method, made by Fabry, Macé de Lépinay, & Perot [24] in cooperation, showed that the dimensions of the cube were 0.24 to 0.40 μ smaller than had been supposed. The most probable cause of the difference is an unrecognized error of about 4×10^{-6} in the index of refraction of the quartz.

Other index measurements of good or fair precision, made with sodium light, are included in Table XXXI.5 and are compared with those already mentioned, as well as with data from tables on subsequent pages. The indices are indices in air at the temperature of the specimen (see p. 603).

Various measurements of lower precision are also available, but do not add anything to the information already recorded here.

The best experimental data on the relation of refraction to frequency in quartz

Refractometry is a field in which there has been striking instrumental progress in the last four decades. As a result, we can now easily measure an index of refraction with a precision of 1 in the fifth and even of 5 in the sixth decimal place, when the index is of the order of 1.5.

It will be evident from the data on the constancy of the index of quartz, presented in the first part of this chapter, that an apparent accuracy of 1 in the sixth place is an illusion, since we know that the index is not reproducible, from specimen to specimen of clear colorless quartz, closer than 2 in the fifth and possibly 1 in the fourth place. Nevertheless, in the study of the relation of refraction to frequency, a precision of 1 in the sixth is highly desirable, and the results have lent themselves remarkably to theoretical treatment. This matter of theoretical interpretation will be taken up in Chapter XXXVII. At present we are concerned with the accuracy of the experimental data and their empirical representation by means of formulas.

As in previous chapters, the distinction between precision and accuracy must be kept in mind. For purposes of figuring lenses and prisms the designer is not so much concerned with the absolute value of the index of refraction at any one frequency as he is with the change of index with the frequency. This relative change can be measured with high precision, in some instances even to 5 in the sixth place, by means of a refractometer such as the Abbe-Pulfrich, although the index itself may not be accurate to closer than 5 in the fifth place. The refractometer method is a comparison method, depending for its accuracy upon the accuracy with which the index of the hemisphere of the refractometer has been determined. It is not well adapted to measurements over a large range of substances or even of frequencies, since it is most precise when the tested substance has an index equal to that of the hemisphere.

[24] Article cited in XVIII, note [3].

TABLE XXXI.6.

EXPERIMENTAL DATA ON THE INDICES OF REFRACTION OF QUARTZ AT ROOM TEMPERATURES. GIFFORD, 1902-1910 (15° C); MARTENS, 1901 (18° C); TROMMSDORFF, 1901.

Radiation	Wavelength mμ	Gifford		Martens		Trommsdorff
		N_ϵ	N_ω	N_ϵ	N_ω	N_ω
Al	185.467	1.690 069	1.675 895	1.689 88	1.675 71	....
Al	186.290	....	....	1.688 08	1.673 98	....
Al	193.58	1.673 488	1.660 027	1.673 37	1.659 90	....
Au **	197.75	....	....	1.666 01	1.652 85	....
Al	198.98	1.663 987	1.650 917	1.663 94	1.650 87	....
Au **	200.06	....	....	1.662 21	1.649 22	....
Zn	202.55	1.658 443	1.645 584	....	....	....
Au	204.448	....	....	1.655 60	1.642 89	....
Zn *	206.31	1.653 037	1.640 398	....	....	....
Au	208.20	....	....	1.650 38	1.637 85	....
Zn	210.05 †	1.648 144	1.635 698	....	....	....
Au	211.07	....	....	1.646 67	1.634 28	....
Cd 26	214.439	1.642 704	1.630 466	1.642 58	1.630 35	1.630 42
Cd 25	219.462	1.637 022	1.624 991	1.636 95	1.624 90	1.625 04
Cd	223.986	....	....	1.632 31	1.620 45	....
Cd 24	226.503	1.629 965	1.618 198	....	....	1.618 19
Cd 23	231.288	1.625 647	1.614 034	1.625 55	1.613 95	1.614 00
Cd 22	232.115	....	....	....	....	1.613 19
Au	242.796	....	....	1.616 47	1.605 22	....
Ag *‡	244.53	1.615 860	1.604 619	....	....	....
Au	250.329	....	....	1.611 38	1.600 31	....
Cd 18	257.304	1.607 164	1.596 246	1.607 10	1.596 20	1.596 26
Al	263.155	....	....	1.603 86	1.593 06	....
Au	267.595	....	....	1.601 59	1.590 87	....
Cd 17	274.867	1.598 132	1.587 529	1.598 10	1.587 51	1.587 56
Al	281.618	....	....	1.595 16	1.584 67	....
Au	291.358	....	....	1.591 34	1.580 96	....
Cd 15	298.062	....	....	....	....	1.578 64
Sn	303.412	1.587 231	1.576 992	....	....	....
Al	308.216	....	....	1.585 64	1.575 47	....
Au	312.279	....	....	1.584 45	1.574 31	....
Cd ‡‡	325.253	....	....	....	....	1.570 82
Zn *	330.28	1.579 729	1.569 742	....	....	....
Cd 11	340.365	....	....	1.577 37	1.567 47	1.567 39
Cd 10 *	346.69	....	....	....	....	1.566 21
Al	358.681	....	....	1.573 69	1.563 90	....
Cd ‡‡	361.25	1.573 243	1.563 473	....	....	1.563 46
Al	394.403	....	....	1.568 05	1.558 46	....
Al	396.154	1.567 836	1.558 235	....	....	....
Cd 8	398.82	....	....	....	....	1.557 91
Hg	404.656	1.566 711	1.557 151	....	....	....
Hγ	434.047	1.563 406	1.553 976	1.563 39	1.553 96	....
Hg	435.834	1.563 227	1.553 797	....	....	....
Cd 7	441.568	....	....	1.562 64	1.553 24	1.553 18
Cd 6	467.815	....	....	1.560 34	1.551 02	1.551 00
Cd 5	479.991	1.559 449	1.550 132	....	....	1.550 14
Hβ	486.133	1.558 988	1.549 700	1.558 97	1.549 67	....
Cd 4	508.582	1.557 479	1.548 236	1.557 46	1.548 22	1.548 21
				1.557 46 ‖	1.548 22 ‖	
Fe *	526.995	1.556 388	1.547 177	....	....	

TABLE XXXI.6. (*Continued*)

Radiation	Wave-length mμ	Gifford		Martens		Trommsdorff
		N_ϵ	N_ω	N_ϵ	N_ω	N_ω
Cd 3	533.85	....	....	1.555 99 1.555 99 ‖	1.546 80 1.546 80 ‖	1.546 79
Cd 2	537.89	....	....	....	....	1.546 50
Hg	546.072	1.555 339	1.546 168	1.555 34	1.546 17	....
Pb *	560.88	1.554 619	1.545 475	1.554 61	1.545 46	....
Na *	589.29	1.553 366	1.544 256	1.553 35	1.544 24	....
Au	627.82	....	....	1.551 86	1.542 80	....
Cd 1	643.847	1.551 353	1.542 309	1.551 31 1.551 31 ‖	1.542 27 1.542 26 ‖	1.542 24
Hα	656.278	1.550 948	1.541 931	1.550 91	1.541 89	....
Li	670.786	1.550 472	1.541 459	1.550 47	1.541 45	....
He *	706.520	1.549 487	1.540 500	....	....	....
K *	768.19	1.547 997	1.539 060	1.547 94	1.539 03	....
Rb	794.763	1.547 421	1.538 513	....	....	....

* Mean intensity.

** Originally listed as Al.

† Dr. MERWIN suggests that this wave-length, from Kayser's tables, is probably slightly in error, since the indices of quartz, vitreous silica, and fluorite, by two observers, fall out of line to the same proportional extent.

†† Listed as "Cd 12" in original, but cannot be Cd 12 as identified by Kayser, Vol. V.

‡ This group of lines is evidently wrongly identified, as the points fall very far out of line. The points are therefore omitted from the curves of Figures XXX.6, XXXI.1, and XXXI.2.

‡‡ Probably mean intensity of 3 lines.

‖ Measurements with new 1-second spectrometer.

Certain other methods can also be adapted to the securing of precise relative values.

The limits to the absolute measurement of the index are evident from the fact that an error of 3 seconds in the angle of a 60° prism or in the measurement of the deviation produced by it, when the index is about 1.5, is equivalent to 0.000 01 or 10×10^{-6} in the index, while every-day measurements of angles have a precision of only about 10 to 30 sec. It takes a circle of astronomical quality to yield a real accuracy of 1 sec. On the effects of temperature and pressure of the air, see p. 604.

The most precise and accurate sets of measurements covering a range of frequencies are those by Gifford (1902-1910), Martens (1901), Carvallo (1898), Paschen (1911), Müller (1885), Macé de Lépinay (1887), and Trommsdorff (1901). Table XXX.2, containing the most probable indices, is based mainly on the data of these investigators. Gifford, Martens, and Trommsdorff were concerned principally with the visible and ultra-violet; Müller and Macé de Lépinay with the visible only; and Paschen and Carvallo with the ultra-red.

Gifford's measurements on quartz and vitreous silica were made on accurately cut equilateral triangular prisms, and settings on the three angles in succession practically eliminated the error of the angle of the prism, which is usually the largest error in an absolute index measurement. Measurements were made at 26 frequencies in the visible and ultra-violet,[25] to which 7 additional visible frequencies were subsequently added.[26] A Hilger quartz spec-

TABLE XXXI.7.

PASCHEN'S MEASUREMENTS OF THE ORDINARY REFRACTIVE INDEX N_ω OF QUARTZ AT 18° C.

Radiation	Wave-length mμ	Optical measurements	Bolometric measurements against He 587.56 or Hg 546.07	Bolometric measurements by Langley's method
Hg	546.072	1.546 172	....	....
He	587.563	1.544 308	....	....
Na	589.29	1.544 239	....	....
O	615.75	1.543 234	....	....
He	667.815	1.541 546	1.541 545	....
He	706.520	1.540 484	1.540 490	....
He	728.135	1.539 950	1.539 954	....
	736.65	....	....	1.539 74
K	766.494	1.539 076	....	....
O	777.33	....	1.538 840	....
	785.76	....	....	1.538 68
O	844.67	....	1.537 527	....
	883.98	....	....	1.536 85
	982.20	....	....	1.535 33
Hg	1014.06	....	1.534 857	....
He	1083.04	....	1.533 900	....
Hg	1128.82	....	1.533 287	....
	1178.64	....	....	1.532 63
	1473.30	....	....	1.528 79
Hg	1529.61	....	1.528 030	....
	1767.96	....	....	1.524 64
He	2058.20	....	1.520 008	....
	2062.62	....	....	1.519 91
	2357.28	....	....	1.514 49
	2651.94	....	....	1.508 24
	2799.27	....	....	1.504 74
	3093.93	....	....	1.497 03

trometer divided to 1 second was used. 36 settings were made at each frequency for each index. The results on quartz, which are indices at 15° in air at 15°,[27] are given in Table XXXI.6. The values for quartz are estimated by the author to be correct in the fifth decimal and approximately correct in the sixth.

The most extended measurements of the index of quartz in the ultra-

[25] GIFFORD, J. W., article cited in note [1].
[26] GIFFORD, J. W., Proc. Roy. Soc. London (1910) A **84**: 193.
[27] GIFFORD, J. W., Proc. Roy. Soc. London (1922) A **100**: 621-626.

violet are those of Martens.[28] He used 40 frequencies of radiation from various metallic spark spectra, mercury and hydrogen vacuum tubes, and luminous flames. The indices were measured, part photographically, on a prism of left-quartz, by the method of the known angle of incidence. The

TABLE XXXI.8.

INDICES OF REFRACTION OF QUARTZ AT 18°,* IN AIR. CARVALLO, 1898.

Wave-length mμ	Plate	N_ϵ	N_ω
598.55	I	1.552 98	....
615.67	I	1.552 31	....
633.68	I	1.551 67	....
652.86	I	1.551 03	....
673.1	I	1.550 41	1.541 39
695.0	I	1.549 78	1.540 78
718.5	I	1.549 15	1.540 17
743.5	I	1.548 52	1.539 56
771.1	I	1.547 89	1.538 95
800.7	I	1.547 25	1.538 34
832.5	I	1.546 61	1.537 73
867.1	I	1.545 98	1.537 12
904.7	I	1.545 32	1.536 49
946.0	I	1.544 64	1.535 83
991.4	I	1.543 92	1.535 14
1041.7	I	1.543 17	1.534 42
1097.3	I	1.542 38	1.533 66
1159.2	I	1.541 52	1.532 83
1228.8	I	1.540 57	1.531 92
1307.0	I	1.539 51	1.530 90
1319.5	II	....	1.530 76
1368.5	II	1.538 69	1.530 11
1395.8	I	1.538 32	1.529 77
1421.9	II	1.537 96	1.529 42
1479.2	II	1.537 16	1.528 65
1497.2	I	1.536 92	1.528 42
1541.4	II	1.536 30	1.527 81
1608.7	II	1.535 29	1.526 87
1614.6	I	1.535 24	1.526 79
1681.5	II	1.534 22	1.525 83
1748.7	I	1.533 19	1.524 85
1761.4	II	1.533 01	1.524 68
1848.7	II	1.531 63	1.523 35
1945.7	II	1.530 04	1.521 84
2053.1	II	1.528 23	1.520 05
2171.9	II	1.526 09	1.517 99

* According to correspondence with the author.

first set was made on spectrometers with 2″ and 10″ sensitivity, and these were afterwards satisfactorily checked[29] visually on 5 frequencies on a spectrometer of 1″ sensitivity. The results are included in Table XXXI.6. (See pp. 617-618.)

[28] MARTENS, F. F., *Ueber die Dispersion ultravioletter Strahlen*, Ann. d. Physik (1901) (4) **6**: 603-640.

[29] MARTENS, F. F., Ann. d. Physik (1902) (4) **8**: 459-465.

The most precise measurements of the refractive index of quartz in the ultra-red region (though only for N_ω) seem to be those of Paschen.[30] Having developed constant sources of radiation, and possessing exact data on the wave-lengths, he was able to make bolometric readings on both visible and ultra-red radiations and to use the method customarily employed in the visible region, obtaining results significant in the sixth decimal place. Measurements were made on a Cornu prism at frequencies from wave-length 546.07 mμ out to 3093 mμ. The results are given in Table XXXI.7.

Another extended and precise set of measurements on the refraction of quartz in the near ultra-red is that of Carvallo.[31] These were made by Mouton's method (see p. 632), at 36 frequencies, between wave-lengths of 599 and 2172 mμ, part on one plate of quartz and part on another. The results, which are given in full in Table XXXI.8, have a precision of about 10×10^{-6}. Coblentz[32] considers that in the ultra-red the results of Carvallo are slightly more accurate than those of Paschen.

Trommsdorff[33] measured the refraction of quartz (ordinary ray) and vitreous silica, using Abbe's autocollimation method for the visible spectrum, and the method of perpendicular incidence, but with photographic recording, for the ultra-violet. This was checked on quartz by the use of the fluorescence method with direct observation. Measurements were made on the ordinary ray of quartz at 20 frequencies from 214 to 644 mμ. By differential measurement a precision of about 20×10^{-6} was obtained. The results on quartz are included in Table XXXI.6.

Pérard[34] made accurate determinations of the ordinary refractive index of quartz for 4 visible frequencies over the range 5 to 23°, as an incidental result of a set of measurements on the quartz length-standards of the International Bureau of Weights and Measures (see p. 830). Within the limits stated, the change of index with temperature is linear. The results on the 10-mm standard are:

Radiation	Wave-length (mμ)	n_ω (absolute)	N_ω at 18° in air at 18°
Hg	435.834	$1.554\,311 - 5.56 \times 10^{-6}t$	1.553 781
Hg	546.072	$1.546\,689 - 5.85 \times 10^{-6}t$	1.546 160
Hg	579.066	$1.545\,179 - 5.96 \times 10^{-6}t$	1.544 649
Cd	643.847	$1.542\,801 - 6.15 \times 10^{-6}t$	1.542 269

The precision is about 3×10^{-6}.

Some very precise measurements of the refractivity of quartz for ultra-red radiation out to 2.9 μ have been made at the Reichsanstalt by Schönrock, but are awaiting an accurate determination of the errors of the screw of the spectrometer before being reduced to final form for publication.

[30] Paschen, F., *Über die Dispersion des Quarzes im Ultrarot*, Ann. d. Physik (1911) (4) **35**: 1005-1008.

[31] Carvallo, E., *Recherches de précision sur la dispersion infra-rouge du quartz*, Compt. rend. Acad. Sci. Paris (1898) **126**: 728-731.

[32] Coblentz, W. W., Sci. Papers Bur. Standards (1920) **16**: 701-714 (No. 401).

[33] Trommsdorff, H., article cited in XXX, note [10]. (Diss., Jena, 1901.)

[34] Pérard, A., *Deux méthodes pour la détermination des étalons primaires en quartz*, Journ. de Physique (1922) (6) **3**: 252-260.

Solar frequencies

Measurements of good precision have also been made with sunlight as the source of radiation, dispersed by means of prism or grating. The chief difficulty with sunlight is in the identification of the frequencies employed. The solar spectrum is so packed with lines, of every grade of intensity and spacing, that its aspect changes with every change in the kind or degree of dispersion to which it is subjected. Hence measurements using sunlight are less satisfactory than those using controlled laboratory sources, not from any loss of precision, but from loss of reproducibility.

TABLE XXXI.9.

REFRACTIVE INDICES OF QUARTZ AT ROOM TEMPERATURES. VAN DER WILLIGEN, 1870.

Radiation	Wave-length mμ	N_ϵ		N_ω	
		Quartz II 23.80°	Quartz III 16.80°	Quartz II 23.60°	Quartz III 16.00°
51α (H)	396.848	1.567 69	1.567 66	1.558 11	1.558 13
50	403.29	1.566 81	1.566 78	1.557 30	1.557 24
46 (Hδ)	410.174	1.565 97	1.565 93	1.556 47	1.556 43
43 (g)	422.67	1.564 53	1.564 47	1.555 08	1.555 05
40 (G)	430.79	1.563 65	1.563 62	1.554 22	1.554 21
36β	453.12	1.561 57	1.561 52	1.552 20	1.552 15
35	466.81	1.560 39	1.560 35	1.551 08	1.551 05
34 (F)	486.133	1.558 95	1.558 86	1.549 66	1.549 60
31	495.76	1.558 26	1.558 19	1.549 02	1.548 97
30	504.14	1.557 72	1.557 65	1.548 47	1.548 42
27β (b_4)	516.74	1.556 93	1.556 84	1.547 74	1.547 64
25 (b_1)	518.362	1.556 84	1.556 75	1.547 63	1.547 58
22β	526.8	1.556 33	1.556 27	1.547 15	1.547 10
19	545.56	1.555 33	1.555 25	1.546 17	1.546 08
14αγ (D)	589.29	1.553 29	1.553 23	1.544 19	1.544 14
5 (C)	656.278	1.550 85	1.550 80	1.541 85	1.541 79
4α (B)	687.22	1.549 98	1.549 89	1.540 97	1.540 89
3α (a)	718.9	1.549 10	1.549 04	1.540 18	1.540 09
1α (A)	760.7	1.548 06	1.548 02	1.539 14	1.539 11

The best of the solar measurements are those by van der Willigen (1870), Müller (1885), and Macé de Lépinay (1887).

Van der Willigen[36] measured the two indices of quartz, using the method of minimum deviation at 15 to 19 frequencies in the visible solar spectrum. He employed 3 prisms, on one of which (No. II) measurements were made on all three angles. The temperature was measured to 0.01° and the results reduced to a uniform temperature for each series of frequencies. The results have a precision for prism I of about 40×10^{-6} and for prisms II and III of about 10 to 15×10^{-6}. The data on II and III are summarized in Table XXXI.9.

These results seem to have received less consideration than they deserve, partly because of the author's special notation for the lines used, partly because

[36] VAN DER WILLIGEN, V. S. M., Arch. Musée Teyler (Harlem) (1869) **2**: 153-182; same (1870) **3**: 34-54.

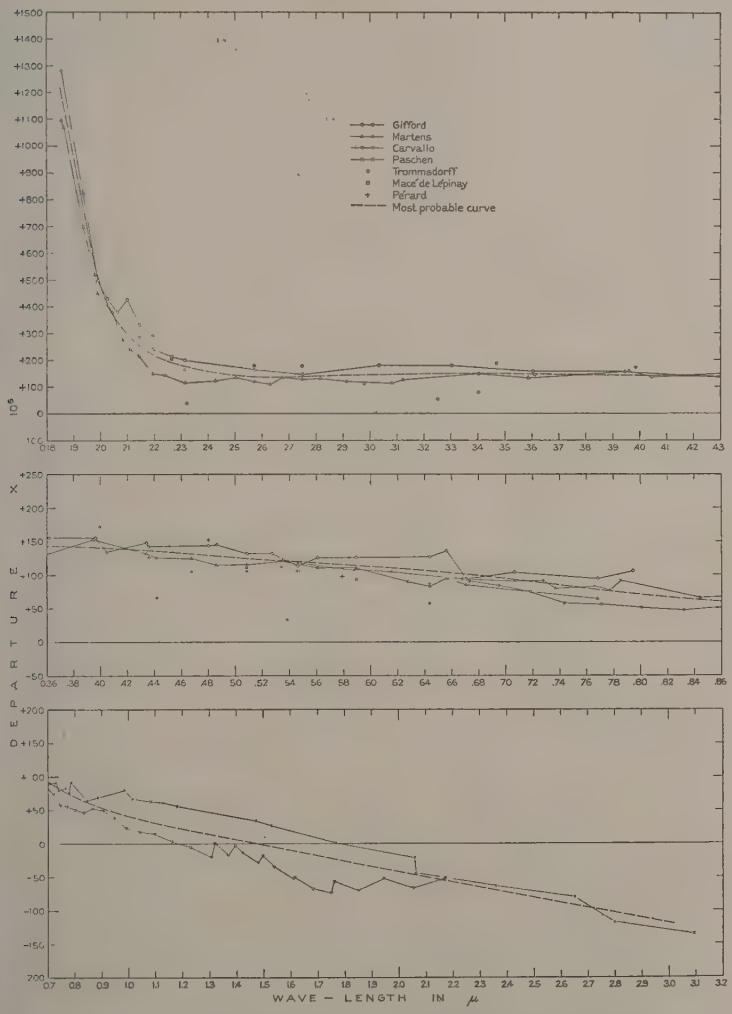


FIG. XXXI.1.—Best experimental data on N_ω, the index of refraction of the ordinary ray of quartz in air. Ordinates are departures of measured indices from a standard curve (see text). Note that the scale of ordinates for the middle and bottom sections is larger than for the top section.

his wave-lengths, measured at about the same time, are not particularly good. Nevertheless, the indices bear the marks of good precision and accuracy. By a little detective work I have been able to identify all of the lines with fair certainty and without dependence upon the indices themselves, in spite of my slight acquaintance with the solar spectrum, and find on recalculation in terms of modern wave-lengths that the results are nearly equal in relative precision to the best available, though they are uniformly low.

Müller's measurements (1885), at 8 solar frequencies, will be described more fully in Chapter XXXIV.

Macé de Lépinay [37] measured the two indices of quartz for 12 frequencies in the visible solar spectrum, correcting the results to 15°C by means of Dufet's formula (see p. 677), and measuring on all three angles of an equilateral triangular prism, thus eliminating the error of the angles. The precision is about 10×10^{-6} or better.

The data of Müller and of Macé de Lépinay are collected in Table XXXI.10.

TABLE XXXI.10.

INDICES OF REFRACTION OF QUARTZ IN AIR, AT SOLAR FREQUENCIES. MÜLLER, 1885; MACÉ DE LÉPINAY, 1887.

Radiation Solar line	Wave-length mμ	N_ϵ Müller	N_ϵ Macé	N_ω Müller	N_ω Macé
K	393.367	....	1.568 21	....	1.558 61
H	396.848	1.567 73	1.567 75	1.558 16	1.558 16
h (Hδ)	410.174	1.566 05	1.566 04	1.556 50	1.556 50
G′ (Hγ)	434.047	1.563 40	....	1.553 95	....
*f	432.578	....	1.563 57	....	1.554 13
F	486.133	1.558 96	1.558 99	1.549 67	1.549 69
b_1	518.362	1.556 86	1.556 89	1.547 63	1.547 66
E	527.00 (?)	....	1.556 40	....	1.547 17
D	589.29	1.553 34	1.553 36	1.544 23	1.544 25
C (Hα)	656.278	1.550 92	1.550 93	1.541 88	1.541 90
B	687.2	1.549 99	1.550 00	1.540 99	1.541 00
a	718.9	....	1.549 15	....	1.540 17
A	760.7	....	1.548 13	....	1.539 19

* Called G′ by MACÉ (and also by DUFET in his *Données numeriques*, 1900).

COMPARISON AND EVALUATION OF THE DATA

The measurements summarized in the preceding pages are of so high a precision that differences among them cannot be brought out by a direct plot of index against wave-length, or even of departures of the index from some simple function. Although a considerable amount of calculation is required, I have found it best to calculate and plot the departures of the measured indices from representative dispersion formulas. For the ordinary index the formula of Rubens, modified slightly in the third term, was used:

$$N^2_\omega = 3.4269 + \frac{0.010654}{\lambda^2 - 0.010627} + \frac{111.49}{\lambda^2 - 100.77}$$

[37] MACÉ DE LÉPINAY, J., *Indices du quartz dans le spectre visible*, Journ. de Physique (1887) (2) **6**: 190-196.

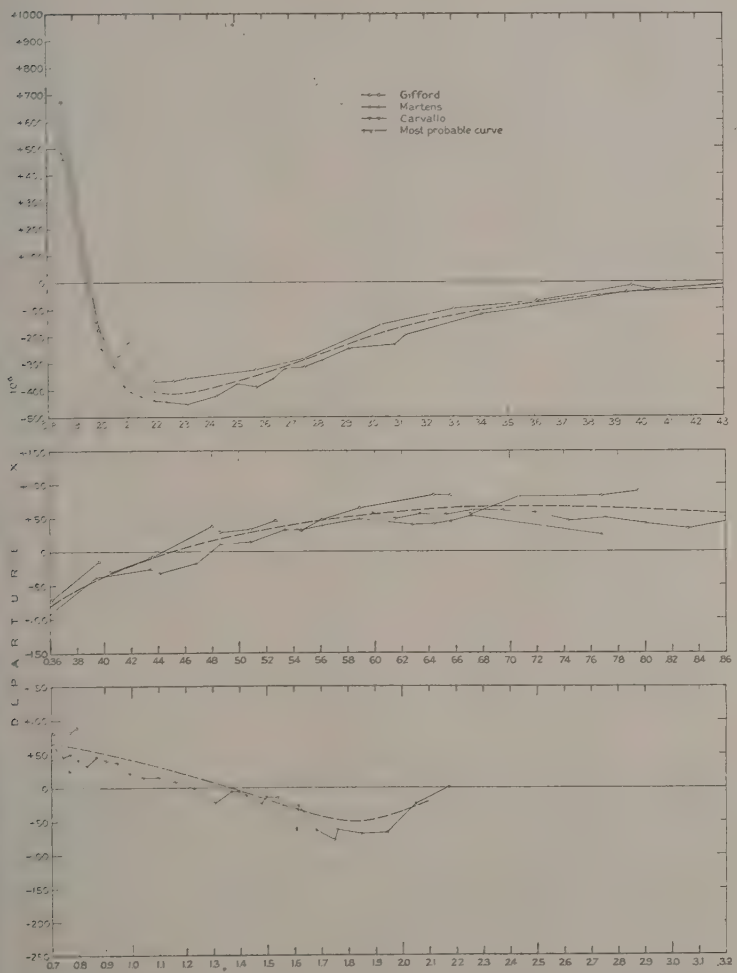


FIG. XXXI.2.—Best experimental data on N_ϵ of quartz. See legend to preceding figure.

Departures of the observed values from this curve are plotted on a considerably magnified scale in Figure XXXI.1, which contains the data of Gifford, Martens, Paschen, Carvallo, Trommsdorff, and Pérard.

A similar reference curve for N_ϵ was obtained [38] by finding the differences of all the calculated values of N_ω from a selected minimum (at $\lambda = 2.172\ \mu$), multiplying the differences by the constant factor 1.043, and adding them to the corresponding minimum value of N_ϵ. Departures of the observed data from this curve are plotted in Figure XXXI.2.

The shapes of these curves are not of importance, as they will vary with small changes in the constants of the formula. What they are

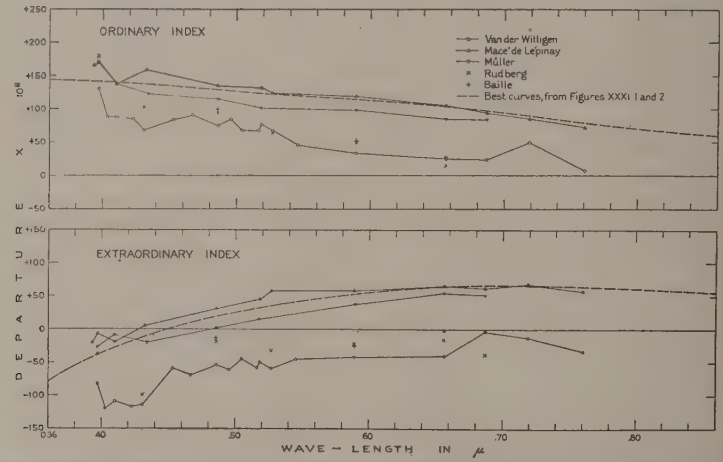


FIG. XXXI.3.—Best experimental data on the indices of quartz as determined with solar lines.

intended to bring out is the degree of agreement, as well as the internal consistency, in the various experimental series. Gifford's and Martens' show the best precision but differ systematically. Trommsdorff's are somewhat scattering. Carvallo's are systematically lower than Paschen's.

Frequent instances of parallelism between the two curves (N_ϵ and N_ω) emphasize what was said at p. 592 to the effect that the precision of the indices is sometimes better than that of the wave-lengths.

The data on the solar lines, namely, of van der Willigen, of Müller, and of Macé, are similarly shown in Figure XXXI.3, in comparison with the most probable curves deduced from all the data.

For the most exact comparison the data should be reduced to a uniform temperature, both of the quartz and of the air in which it is measured (see

[38] This method was suggested to me by Dr. MERWIN.

p. 604 for the magnitude of the effects). These temperatures fall between the limits 15 and 20°C; 18° is the temperature usually taken for comparison, although the standard wave-lengths are referred to air at 15°. But the temperature-coefficients of the indices of quartz are not known over the entire range of frequencies; furthermore it is evident from the direction and magnitude of the differences between the sets that these differences are not due to temperature alone. Hence it has seemed best to plot the data just as they stand, the differences of temperature being kept in mind in placing the curves of most probable values.

TABLE XXXI.11.

INDEX OF REFRACTION OF QUARTZ FOR ORDINARY RAY, AT 19° C. RUBENS, 1894-1895.

Radiation	Wave-length, μ	N_ω
K	0.404 57	1.557 050
H	0.434 047	1.553 869
H	0.486 133	1.549 606
Ca	0.534 946	1.546 633
Na	0.589 29	1.544 147
H	0.656 278	1.541 807
K	0.768 19	1.538 930
	1.160	1.532 9
	1.617	1.527 1
	1.969	1.521 6
	2.327	1.515 6
	2.59	1.509 9
	2.84	1.503 9
	3.03	1.498 5
	3.18	1.494 2
	3.40	1.487 7
	3.63	1.479 0
	3.80	1.473 9
	3.96	1.467 8
	4.09	1.461 9
	4.20	1.456 7

These "most probable" curves, as drawn, contain slight humps and hollows for which there is no theoretical justification, but the attempt has been made to get the best representative curve as a purely experimental problem, without regard to theory.

The departures as plotted in Figures XXXI.1 and 2 have been satisfactorily checked by comparison with departures calculated in an entirely different way by Dr. Merwin (see p. 598).

The farther ultra-red

Beyond a wave-length of 3 μ we have the results of Rubens and his coworkers. Exact measurements extending the dispersion spectrum of quartz to 4.2 μ were made by Rubens[39] in 1894 and republished[40] in 1895 with the

[39] RUBENS, H., Ann. d. Physik u. Chem. (1894) **53**: 267-286.

[40] RUBENS, H., *Die Ketteler-Helmholtz'sche Dispersionsformel*, Ann. d. Physik u. Chem. (1895) **54**: 476-485.

more reliable wave-lengths derived from Paschen's experiments. Rubens' measurements were made by Langley's method, the radiation being dispersed by a grating of gold wire in a spectrometer and then sent through a prism of the substance in a second spectrometer provided with a sensitive bolometer. Readings were made at 7 visible frequencies with an estimated precision of 5×10^{-6} in the index, and then at 14 ultra-red frequencies up to 4.20 μ. The readings were differential, basing upon the sodium doublet. The final values of N_ω are given in Table XXXI.11. The precision is not as high as that of the later measurements of Carvallo and of Paschen, but the frequencies extend a little farther into the ultra-red.

Beyond 5 μ the transparency of quartz diminishes rapidly with increasing wave-length, becoming practically zero at certain wave-lengths (see XXXV). Indices of refraction in this region are not determinable directly, but can be calculated from the reflecting power. Another region of increasing transparency then follows, into which Rubens & Aschkinass [41] extended direct observations of refraction.

Using thin-edged prisms of quartz, they obtained the values shown below for the intermediate transmitted radiation which appeared most strongly absorbed by a 4-mm plate of rock salt:

Quartz prism angle	Minimum deviation at absorption-maximum	N_ω
6° 2′	7° 6′	2.18
10° 9′	12° 16′	2.19

The value obtained with the sharper prism is the more reliable. The wave-length of the radiation yielding the above data was determined by means of a grating to be 56 μ.

The refractive index of quartz for Hertzian waves of wave-length 57.2 mm (frequency 5.24×10^9) was more accurately measured by Rubens [42] in 1917, by an interference method. The method was not direct, but comparative, the refractive index of a reference standard of sheet glass (as used for photographic plates) being first determined, and the unknown being then compared with this standard. The index of the standard glass as determined by two different interference methods was 2.606 and 2.630, respectively, and the standard value was taken as 2.620. The results, with a thickness of 10.96 mm of quartz, for the ordinary ray, were 7.50 and 7.36 mm as the equivalent thicknesses of glass, measured in opposite directions from the standard interference position. The mean is 7.43, from which the index N_ω of quartz is 2.10. From the data given above it is evident that the accuracy is of the order ± 0.02 in 2.10.

[41] Rubens & Aschkinass, *Isolirung langwelliger Wärmestrahlen durch Quarzprismen*, Ann. d. Physik u. Chem. (1899) 67: 459-466.

[42] Rubens, H., *Über die Brechungsexponenten einiger fester Körper für kurze Hertzsche Wellen*, Sitzungsb. K. Preuss. Akad. Wiss. Berlin, 1917: 556-567.

The few data just given are the only direct measurements of indices in the region beyond 4 μ. Over most of the range, at least from 5 to 40 μ, direct determinations would be difficult to make because of the strong reflection and absorption. The indices can, nevertheless, be calculated with reasonable certainty from the reflecting power of the substance for frequencies not too near an absorption band.

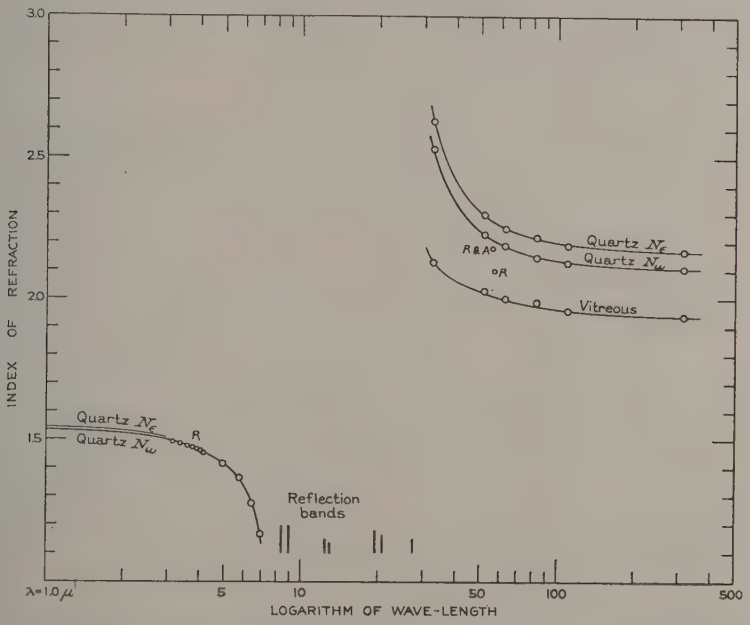


FIG. XXXI.4.—Experimental data on the refractive indices of quartz and vitreous silica in the ultra-red beyond the range of Figures XXXI.1 and XXXI.2. Smaller circles are indices based on measurements of refraction: R = Rubens, R & A = Rubens & Aschkinass. Larger circles are indices calculated from reflecting power.

Some indices calculated from reflecting power are collected in Table XXXI.12.

The following indices,[43] calculated from the reflecting power of quartz for the residual rays of rock salt and sylvite (KCl), are also on record, but are not in especially good agreement with the rest, perhaps because of inhomogeneous radiation (see p. 712):

Wave-length	n_ω
51.7 μ	2.46
63.4 μ	2.12

[43] RUBENS, H., & ASCHKINASS, E., *Die Reststrahlen von Steinsalz und Sylvin*, Ann. d. Physik u. Chem. (1898) **65**: 241-256.

The indices directly measured and those calculated from reflection, both for quartz and for vitreous silica, at wave-lengths beyond 3 μ, are shown graphically in Figure XXXI.4. Although Rubens' value of $N_\omega = 2.10$ appears rather far off the calculated curve, the agreement is in fact quite satisfactory when we consider that this is a comparison between indices obtained from two widely different sources: one, a partly theoretical calculation from the reflection of heterogeneous heat waves sent out by a gas-burner; the other, the measured deviation, by a prism, of homogeneous electric waves sent out by an electric oscillator.

TABLE XXXI.12.

REFRACTIVE INDICES OF QUARTZ AND VITREOUS SILICA FOR ULTRA-RED RADIATION, AS CALCULATED FROM REFLECTING POWER. RUBENS & NICHOLS, 1897 (FOR 5 TO 7 μ); RUBENS, 1916.

Wave-length μ	Quartz		Vitreous silica
	n_ω	n_ϵ	n
5.0	1.417		
5.8	1.368		
6.45	1.274		
7.0	1.167		
33	2.53	2.63	2.13
52	2.23	2.30	2.03
63	2.19	2.25	2.00
83	2.15	2.22	1.99
110	2.13	2.19	1.96
313	2.11	2.17	1.94
∞	2.11	2.15	1.94

Earlier and less accurate measurements on the relation of refraction to frequency

Many of the earlier sets of measurements of refractive index were of fairly good precision and accuracy, although not equal to those just listed. For purposes of discussion they may be grouped as follows:

(a) Measurements mainly in the visible solar spectrum: Rudberg (1828), Schrauf (1860), Baille (1867), Mülheims (1888).

(b) Measurements extending into the ultra-violet: Esselbach (1856), Mascart (1864), Sarasin (1878), Simon (1894).

(c) Measurements extending into the ultra-red: Mouton (1879), Rubens (1892), Moreau (1893).

Early measurements in the visible spectrum

The first measurement of the refractive indices of quartz was made by Malus about 1811. This was before the discovery of the solar spectrum lines by Fraunhofer, so that although Malus obtained fairly precise values for the two indices, he had no way of defining the frequency.

The first measurements of the variation of the refractive indices of quartz with the frequency were made by Rudberg[44] in 1828. After nearly one hundred years these still rank as fairly high-grade measurements. They were made by the minimum-deviation method on two prisms of about 45° angle, with sunlight as the source. The precision is about 50×10^{-6}.

Schrauf's series[45] (1860) consisted of 6 sets in all, made with 4 prisms on 5 solar frequencies, at an average temperature of 20°.

Baille,[46] in the course of an extensive and exact series of measurements by the minimum-deviation method on the refraction of glasses, obtained the two indices of quartz at 12°C for 3 solar frequencies, with a precision of about 20×10^{-6}.

Mülheims,[47] using a Pulfrich refractometer, determined the indices of quartz for 7 visible solar frequencies. Two series were made, with two different glass cylinders.

Of the four sets just mentioned, those of Rudberg and of Baille are shown in Figure XXXI.3. The other two are more scattering and are omitted.

Earlier data in the ultra-violet

Measurements on quartz in the ultra-violet were begun by Esselbach[48] in 1856. He measured N_ω for 7 visible and 7 ultra-violet solar lines, the latter by means of fluorescence. His precision was not very high, and the positions of his ultra-violet lines are not well defined.

Mascart[49] introduced the photographic method for the accurate measurement of refraction in the ultra-violet. He used one angle of a 60° prism, with sunlight as source, and made measurements at 17 frequencies. The precision seems to be about 100×10^{-6}. The disadvantages in the use of the solar spectrum (see p. 622) are such that these measurements no longer rank with those made with artificial sources of radiation.

Sarasin[50] was the first to make an accurate series of measurements of the two indices with artificially controlled sources of the ultra-violet. He used the minimum-deviation method with an accurate prism and a spark source for the rays of cadmium, zinc, and aluminum. The precision of the results, which cover 26 frequencies, is better than 100×10^{-6} except for the three aluminum lines which were relatively weak and therefore less exact. The precision is decidedly less than that of the more recent measurements, and Sarasin's results are therefore not included in Figures XXXI.1 and 2.

Simon[51] determined photographically the ultra-violet refraction of the ordinary ray in quartz by means of the method of minimum deviation with perpendicular incidence. He employed a 31-degree prism cut from the same lot of crystals as Rubens' specimens (p. 627). Zinc in a carbon arc served as the source. The lines were identified by means of approximate wave-lengths deter-

[44] Rudberg, F., Ann. Chem. u. Physik (Poggendorff) (1828) **14**: 45-57.
[45] Article cited in note 6.
[46] Baille, J. B., Ann. Conserv. Arts et Metiers (1867) **7**: 184-283.
[47] Mülheims, A., Zeitschr. Kryst. (1888) **14**: 202-236.
[48] Esselbach, E., Ann. Phys. u. Chem. (Poggendorff) (1856) **98**: 513-546.
[49] Mascart, E., Ann. Sci. École Norm. Super. (1864) **1**: 219-262.
[50] Sarasin, E., Arch. sci. phys. nat. (1878) **61**: 109-119.
[51] Simon, H. T., *Ueber Dispersion ultravioletter Strahlen,* Inaug.-Dissert. Berlin, 1894, 54 pp., 3 pls.

mined by the interference method of Ritter and Rubens. The series covers 7 visible and 14 ultra-violet frequencies, from 768 to 202 mμ. The precision is of the order of 50×10^{-6}, but the results in the ultra-violet are higher than those of Gifford and of Martens, and are also more scattering, hence they have not been used in Figures XXX.1 and 2.

Earlier measurements in the ultra-red

Mouton [52] was the first to measure the refractive indices of quartz in the ultra-red. He introduced the interference method generally known by his name, depending upon the measurement of the angular deviations of the Fizeau-Foucault bands produced when white radiation passes through a polarizer, a quartz plate, an analyzer, and a prism. Mouton measured the indices at 5 ultra-red frequencies between 0.9 and 2.1 μ, with additional measurements in the visible region sufficient to assure himself of an accuracy of 100×10^{-6}. Only the ultra-red data were published.

Rubens [53] measured the index for the ordinary ray in quartz with the aid of the interference bands formed when the double ray reflected from two plane glass surfaces very close together is passed through a prism of the substance in a spectroscope. Measurements were made at 4 visible frequencies and at ultra-red frequencies from 0.839 to 2.348 μ.

Moreau [54] determined the indices of refraction of quartz in the ultra-red by the method of Mouton (see above). He used 5 plates of quartz and obtained data for 9 frequencies between 0.842 and 1.715 μ. The precision is about 50×10^{-6}.

All three of these series are lower in accuracy than the data of Carvallo and of Paschen, and are therefore not used in the curves.

Other data on the indices of quartz

Several other sets of measurements should also be mentioned, although the results need not be given in detail, since they would not add anything essentially new to the data already discussed. They are as follows:

Soret (1883) [55]: A series of measurements of the indices of quartz, made for the purpose of testing his newly devised spectrometer, which was based on the Kohlrausch principle of total reflection in an immersion liquid. The results have a precision of about 200×10^{-6}.

Pulfrich (1887) [56]: Pulfrich took Mascart's refractive indices of quartz as part of the basis for determining the refractive index of the glass cylinder of his total reflectometer. His subsequent measurements on quartz at 7 visible frequencies are therefore not wholly independent determinations of the indices, but are rather tests of the precision of the newly developed instrument. The precision was about 100×10^{-6}.

Wülfing (1895) [57]: A series of measurements of the refractive indices of

[52] Mouton, Compt. rend. Acad. Paris (1879) **88**: 1189-1192.
[53] Rubens, H., Ann. Physik u. Chem. (Wiedemann) (1892) **45**: 238-261.
[54] Article cited in XXXIII, note [20].
[55] Soret, C., Arch. sci. phys. nat. (1883) (3) **9**: 5-32.
[56] Pulfrich, C., Ann. d. Physik u. Chem. (Wiedemann) (1887) **30**: 487-502.
[57] Wülfing, E. A., Tschermak's Min. Petr. Mitt. (1895) **15**: 49-76.

quartz, covering 13 frequencies in the visible region. The natural prism faces (angle 60° 0.3′) of a crystal from Herkimer, New York, were used. The precision was about 100×10^{-6}. These measurements were not intended to be a highly exact study of the dispersion of quartz, but were made to test out certain instrumental equipment.

Rinne & Kolb (1910)[58]: A set of measurements at 23° at 10 visible frequencies, made as a basis for a series at higher temperatures (see p. 678).

Reed (1897)[59]: Like Rinne & Kolb's, a series at 4 frequencies, made as a basis for temperature-coefficients.

Viola (1899)[60]: Viola measured the indices of quartz for the D line on 2 prisms with edges parallel to the axis, by the minimum-deviation method (results in Table XXXI.5), and then determined the indices for 7 other solar frequencies differentially on an Abbe-Pulfrich refractometer, as a test of the apparatus.

Phenomena arising from the refractive properties of quartz

The optical phenomena seen under the microscope and in other forms of optical apparatus as a result of the birefringent and rotatory properties of substances such as quartz have always excited the lively interest of optical physicists, partly, no doubt, because of the brilliant colors and the highly complex yet symmetrical patterns which are produced. Their study is a matter of the application of general principles of refraction and interference, and so is outside the scope of this book, devoted as it is to specific properties of a single substance. Nevertheless, since much of the work has been done with quartz, the subject deserves some mention in passing.

In discussing color effects we need first to realize that we are talking of physiological and psychological phenomena, and not of frequencies or energies. The human eye is in some respects a marvellously adapted organ, but in other respects it is one of the poorest physical instruments known, for it can be deceived with the greatest ease. The ear is a very sensitive instrument for analyzing and recognizing frequencies, while a wide variety of combinations of vibrations may all appear as the same color to the eye.

When the peculiarities of sensation, perception, and judgment are allowed for, the optical phenomena prove to be completely explainable in terms of wave-theory, with the quantitative help of the refractive properties discussed in Chapters XXX to XXXIV. The most recent and thorough of the detailed discussions involving quartz is that of Liebisch.[61]

[58] Article cited in VII, note [14].
[59] Article cited in XXXIV, note [11].
[60] Viola, C., Zeitschr. Kryst. (1899) **32**: 305-337.
[61] Liebisch, T., Sitzungsb. Preuss. Akad. Berlin 1916: 870-883; same, 1918: 821-839. Liebisch, T., & Wenzel, A., same, 1917: 3-32, 777-807.

Chapter XXXII. SECONDARY REFRACTIVE CONSTANTS AND OPTICAL ORIENTATION

Even in the most general case, only two sets of data are required in order to state completely the refractive phenomena of a substance under given conditions (see p. 588). They are:

(a) The axes of the index ellipsoid;

(b) The situation of the index ellipsoid with reference to the crystallographic axes.

Tables of these two at various frequencies,—(a) alone is sufficient for many substances, including quartz,—tell all there is to know of the actual phenomena at the measured frequencies and under a fixed temperature and pressure. But there are several other constants, derivable from the above-mentioned data by calculation, which are not only convenient in use but also sometimes independently measurable. These constants, which may be called *secondary* refractive constants, will now be considered. They include:

Birefringence
Optical character
Axial angle, true
Axial angle, apparent
Relative dispersion of indices and of secondary constants.

Birefringence

The difference between any two of the principal refractive indices of a substance (p. 586) is called a *birefringence*. While not an independent constant, its value can often be measured or estimated independently without reference to the actual values of the indices. The birefringence may then be used as a characteristic constant of the substance and its variation with frequency and with temperature may be independently studied.

Birefringence of silica

Quartz, being uniaxial, has only two indices for a given frequency and temperature and hence only one birefringence: $n_\epsilon - n_\omega$.

Low-tridymite and low-cristobalite, being biaxial, have three indices, and hence three birefringences: $n_\gamma - n_\alpha$, $n_\gamma - n_\beta$, and $n_\beta - n_\alpha$, among which, obviously, only two are independent.

The birefringences of all the forms of silicia are relatively small. That of quartz is the largest, being about 0.009 in the visible spectrum. There are many crystalline substances with a birefringence five to twenty times as great as this.

A comparison of the most probable values for sodium light, at room temperature, follows:

	$N_\epsilon - N_\omega$	$N_\gamma - N_\alpha$	$N_\gamma - N_\beta$	$N_\beta - N_\alpha$
Quartz	0.0091	....	....	....
Tridymite	....	0.004	0.0025	0.0015
Cristobalite	....	0.002	?	?

Quartz.—The data on quartz are fully presented at p. 641.

Tridymite.—The birefringences of low-tridymite are uncertain because of the finely twinned and aggregated character of all the available material. The following measurements in sodium light are on record:

Author	$N_\gamma - N_\alpha$	$N_\gamma - N_\beta$	$N_\beta - N_\alpha$
Mallard [1]	0.001 85	0.000 25	0.001 6
Sokolov [2]	0.005	0.003 3	0.001 7

Low-cristobalite.—The birefringences of low-cristobalite are uncertain for the same reason as holds for tridymite, namely, fine twinning and intricate aggregation of the units. The most probable value of the largest birefringence, $n_\gamma - n_\alpha$, is 0.002, but it may show apparent values which are much less than this, down practically to zero. For example, the birefringence of low-cristobalite embedded in silicate glasses is in many specimens barely discernible with the aid of the sensitive-tint plate.[3]

This apparent disappearance of birefringence, or pseudo-isotropy, probably results from the overlapping of lamellae in such a way that they compensate each other.

Some experimental determinations are:

Author	$N_\gamma - N_\alpha$	Reference
Mallard (1890)	0.000 53	Article cited in IV[18].
Wright (1906)	Not over 0.002	Article cited in V[3].
Ramdohr (1920)	0.001 8	Article cited in IV[21].

Birefringence of micro-crystalline silica

From the nature of the material it is obvious that the data on birefringence of micro-crystalline silica can never be highly exact. Perfectly definite results are obtainable, however, if the size of the crystalline units is not too small.

In general, the birefringence of chalcedonic silica (see p. 153) has the order of magnitude characteristic of quartz and tridymite, namely, 0.003 to 0.009.

[1] MALLARD, E., article cited in IV, note [18].
[2] SOKOLOV, V. I., Proc. Imp. Mineral. Soc. St. Petersburg (1906) **44**: 473-482.
[3] BOWEN, N. L., & ANDERSEN, O., Amer. J. Sci. (1914) **37**: 487-500.

Many of the fibers of the negatively-elongated type of fibrous silica (chalcedonite) show a birefringence which varies continuously along the length of the fiber. Michel-Lévy showed that this appearance is due to a twisted structure, in which the bisectrix n_γ, while remaining perpendicular to the axis of the fiber, turns around the axis as one passes along the length. This has the effect of making the apparent birefringence of a fiber vary from a maximum a little larger than that of quartz down to a barely detectable birefringence with a positive bisectrix and very small optic axial angle.

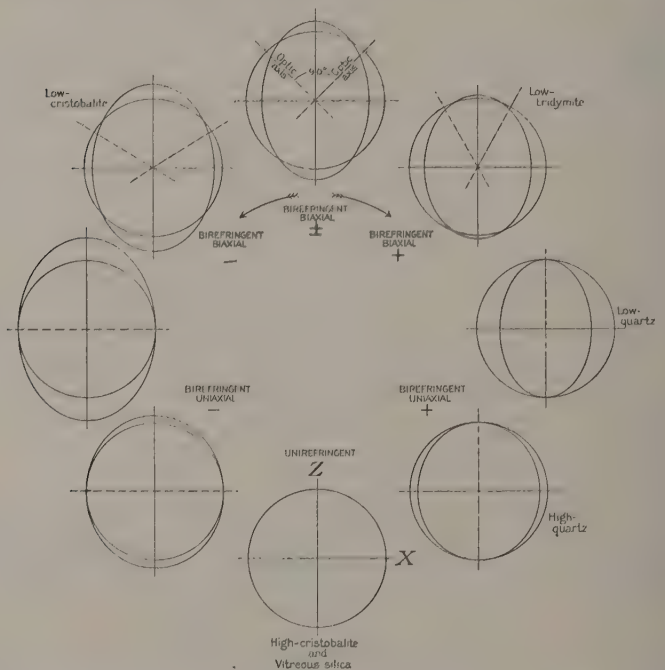


FIG. XXXII.1.—Evolution of birefringent biaxiality into uniaxiality and unirefringency.

Birefringence of dispersed micro-crystalline silica.—Procopiu[4] has measured the degree to which plane-polarized light passing through a liquid in which a finely powdered crystalline substance is suspended is partly depolarized. Powdered quartz fine enough to remain suspended in petroleum depolarizes the light to the extent of 1.1 per cent, while the effect of precipitated calcium carbonate at roughly the same concentration, as regards number of par-

[4] PROCOPIU, S., Compt. rend. Acad. Paris (1921) 173: 409-411.

ticles, is 24 per cent. For a given substance and liquid the effect is proportional to the concentration of the suspended substance.

The depolarizing effect is probably due to the splitting up of the original radiation into two rays each time it traverses or is reflected from a particle, the particles being situated in every possible orientation and thus yielding a certain proportion of light vibrating in all azimuths, that is, unpolarized. This would indicate that the effect should be a function of the birefringence and of the number of particles, and offers a means for studying one of these quantities if the other be known. The method deserves further study, and might be profitably applied to the investigation of the microcrystalline forms of silica whose optical character and birefringence are so difficult to determine.

Optical character

The progression of properties from the most complex case of the *birefringent biaxial* substance, through the *birefringent uniaxial* substance, to the simplest case of the *unirefringent* substance, has already been stated in general terms at p. 585. The corresponding evolution of the index ellipsoid is from the triaxial ellipsoid, through the ellipsoid of rotation, to the sphere.

According to the relation of n_β to n_γ or n_α, birefringent substances are classified as *positive* or *negative*. The meaning of the terms has been stated at pp. 585-588, and is here illustrated again by means of Figure XXXIII.1. This quality of being positive or negative is called the *optical character* of the substance.

Those modifications of silica which are birefringent are grouped, as regards optical character, as follows:

Biaxial positive	$(n_\gamma - n_\beta) > (n_\beta - n_\alpha)$*	Low-tridymite
Biaxial negative	$(n_\beta - n_\alpha) > (n_\gamma - n_\beta)$*	Low-cristobalite
Uniaxial positive	$n_\epsilon > n_\omega$	Low-quartz High-quartz Lower high-tridymite Upper high-tridymite

* These are relations which are approximately true, though not exactly so, when the birefringences are very small, as they are for tridymite and cristobalite.

Like the birefringence, the optical character (positive or negative) is not an independent quality but a secondary or derived quality, calculable if the indices are given. But, again like the birefringence, it can sometimes be determined when the actual values of the indices cannot, and then serves as one of the diagnostic characters of the substance.

Optic axial angle

The two intersecting lines which mark the directions of the optic axes (see p. 586, also Figure XXXII.1) bound two angles. One of these two is bisected by the coordinate axis Z, which is the vibration-direction cor-

responding to the principal index n_γ, and this angle is called the *optic axial angle*[5] or simply the "optic angle". It is usually indicated by the symbol $2V_\gamma$. The other is bisected by the direction corresponding to n_a, and is of course equal to $180° - 2V_\gamma$. It may be indicated by $2V_a$.

The optic axial angle is related to the three indices by the formula:

$$\sin V_\gamma = \frac{n_\gamma}{n_\beta}\left(\frac{n^2_\beta - n^2_a}{n^2_\gamma - n^2_a}\right)^{\frac{1}{2}}$$

Apparent axial angle

The angle between the directions of the two rays of light which have passed while within the crystal along the optic axes, and have then emerged into air from a surface perpendicular to the bisectrix of the optic angle, can be conveniently measured; it is called the *apparent axial angle*, and is usually designated by the symbol $2E$. It bears a simple relation to $2V$, but in the absence of the other data necessary to a calculation of $2V$, the value for $2E$ may be used as a diagnostic constant.

The relation of E to V is given by the formula: $\sin V = n_\beta \sin E$

Tridymite

The optic axial angle $2V_\gamma$ of low-tridymite is about 40°, and the apparent angle about 65°.

Some experimental data are listed in Table XXXII.1.

Table XXXII.1.
Measurements of the Axial Angles of Low-Tridymite.

	Optic axial angle $2V_\gamma$ Degrees	Apparent axial angle $2E_\gamma$ Degrees	Source
Fenner (1912)	35 ± 3	59	
Mallard (1890)	43	66	Natural, Puy-du-Capucin
Wilson (1918)	..	56	Devitrification of soft glass
Sokolov (1906)	72	..	Silica brick
Nikitin[7]	42	..	Natural

Cristobalite

The optic axial angle $2V_\gamma$ of low-cristobalite is large, but indistinct.[6] From its negative optical character it follows that $2V_\gamma$ must be nearer 180 degrees than 0 degrees, but its magnitude is uncertain.

[5] The optic axial angle is sometimes defined as the *acute* angle between the optic axes, and so may be either $2V_\gamma$ or $2V_a$, but the definition given above is the more general, and the one to which the formula applies without qualification.

[6] Wright, place cited in V, note [8].

[7] Nikitin, *Minerals of Bogoslavsky District*, quoted by Sokolov, article cited.

Relation of refractive constants to symmetry

In the preceding part of this chapter we have considered strictly the properties derived from the index ellipsoid of a substance, without considering how the ellipsoid is placed with respect to the axes and planes of symmetry of that substance. In many substances the ellipsoid is automatically set in position by the elements of symmetry and can have no other position, while in a few others it has to be adjusted by the specification of additional constants. In either event, certain phenomena result from the relation of ellipsoid to symmetry which can be independently observed without requiring a knowledge of other constants. Such are the extinction-angles and the optical character of preferred directions.

Optical character of the elongation

When a birefringent substance appears in characteristically elongated growth-forms or cleavage fragments, there may be determinative significance in knowing whether the ray vibrating parallel to this apparent elongation has the greater or the less refractive index. The *elongation* of the crystals or fragments is said to be *positive* when the vibration-direction of the ray of *greater* refractive index (slower speed) approaches parallelism with the longest dimension of the piece; and *negative,* when the vibration-direction of *less* refractive index approaches parallelism with the longest dimension. This quality, more definitely called the *optical character of the elongation,* is a very different kind of "optical character" from that described at p. 637, the optical character of the substance.

Extinction-angles

Another feature which is even less specific than the foregoing, but which is easy to observe with the polarizing microscope and is useful in identifications, is the *extinction-angle.* It results from the non-coincidence of some designated crystallographic direction with one or other of the planes of vibration of polarized light in the substance.

When one or the other of the vibration-directions coincides with the designated crystallographic direction in the substance, the *extinction* is said to be *parallel.* This quality may evidently be recognized even though the indices remain unknown, and though the positions of the crystallographic axes be unknown. If the vibration-direction departs from the designated direction, the extinction is called *oblique* or *inclined.*

Elongation and extinction in silica

Quartz growing in its customary prismatic habit shows positive elongation and parallel extinction.

Plates of low-tridymite when seen on edge look like laths, and have an extinction strictly parallel to the elongation of the laths. The vibration-

direction for index n_a is parallel to this elongation, and the elongation is therefore negative.[8]

Optical characters of micro-fibrous silica

In Chapter X a tentative classification was made of micro-crystalline fibrous silica on the basis of optical character of the substance and optical character of the elongation. The preceding paragraphs will help to make clear the grounds for the classification. It may be supplemented here by a brief historical note.

Rosenbusch made *negative elongation* the distinguishing criterion for what he would call "chalcedony". Michel-Lévy showed that although the elongation might be negative, the substance itself is biaxial and optically *positive*. Further, he found that some new varieties of silica discovered by Munier-Chalmas were also optically positive, but they failed to qualify as Rosenbuschian chalcedony because they proved to be of *positive elongation*. (These varieties were subsequently subdivided into quartzine and lutecite.) Finally, Lacroix in 1900 contributed to the collection an optically *negative* fibrous silica, in this respect unlike any of the foregoing, but of *negative elongation* like Rosenbusch's chalcedony. Only a negative fibrous silica of positive elongation was lacking to complete the confusion, and this appears to be supplied by the birefringent ribbons observed by Rayleigh in vitreous silica (see p. 138).

In reality there is no confusion, if we simply take account of the fact that we are dealing with two independent qualities, and observe that there are four possible combinations of the two (see Table X.1).

Dispersion

Although reference is repeatedly made in scientific literature to "the dispersion" of a substance, there is no quantitatively defined constant answering to that name. The word is used in its most general sense to indicate our summarized knowledge of the relation between a radiational constant and the frequency (or the wave-length) of the radiation. "The dispersion of the rotatory power," "the dispersion of the birefringence," or "the dispersion of the index of refraction" are therefore properly used terms, which refer in a general way to the information contained in a table or curve of rotatory power against wave-length, birefringence against wave-length, index of refraction against wave-length, etc.

The term "dispersion of quartz," as usually employed, means the "dispersion of the indices of refraction of quartz".

Relative dispersion

A definite quantitative meaning can be given, however, to the term *relative dispersion*. This is the general name for the ratio:

[8] Fenner, article cited in IV, note [32]; Sokolov, article cited.

Change of a radiational property with frequency
Some measure of the property itself

Usually the change is measured between the two frequencies corresponding to the Fraunhofer solar lines C and F, and the intermediate frequency at which the property is measured and to which the change is related is taken at the sodium line, D. A further convention is to invert this ratio, defining a *reciprocal relative dispersion.*

The reciprocal relative dispersion of the refractive index, usually called simply "reciprocal relative dispersion" or *constringence* [9] and indicated in optical-glass literature by the symbol ν, is defined by the formula

$$\nu = \frac{N_D - 1}{N_F - N_C}$$

that is, it is the ratio between the refractivity at line D and the change of refractivity between lines F and C.

The values of constringence at 18 to 20° for quartz and vitreous silica, as derived from the data of Table XXX.2, are given in Table XXXII.2, and are compared with values calculated from the best original data on the indices, as given in XXX and XXXI.

TABLE XXXII.2.

CONSTRINGENCE (RECIPROCAL RELATIVE DISPERSION OF THE REFRACTIVE INDEX) OF QUARTZ AND VITREOUS SILICA.

Author	Quartz, extraord. ray	Quartz, ord. ray	Vitreous
(Best value)	68.7	69.9	67.6
Gifford	68.83	70.05	67.92
Martens	68.65	69.95	....
Van der Willigen	68.47	69.68	....
Müller	68.82	69.86	....
Macé de Lépinay	68.66	69.87	....
Riedel	....	....	67.72
Trommsdorff	....	....	67.72
Abbe	....	....	67.83

THE EXPERIMENTAL DATA ON BIREFRINGENCE OF QUARTZ

Macé de Lépinay [10] has made the most extended series of direct determinations of the birefringence of quartz. Measurements were made at 16 solar frequencies from 310 to 688 mμ, each over a series of 8 to 15 temperatures between 1 and 45°C. An interference method was used. The preliminary values [11] published in 1885 are a little lower than the final set, perhaps as a result of inexactness of orientation of the faces of the quartz plate with respect

[9] EVERETT, J. D., in transl. of Hovestadt, *Jena glass* (1902, London): p. 412.
[10] MACÉ DE LÉPINAY, J., *Sur la double refraction du quartz,* Ann. Fac. des Sciences Marseille (1891) 1: 5-18. Journ. de Physique (1892) (3) 1: 23-31.
[11] J. de Physique (1885) (2) 4: 159-166.

to the optic axis. The author also suggests that there may have been a real difference, since the specimens were from different sources.

The precision of the results is better than 1×10^{-6}. The error due to orientation of the faces in the final set of data is shown to be about 0.01 per cent of the birefringence or about 1 in the sixth place.

The results are given in Table XXXII.3, to which I have added a column giving calculated values at 18°, for comparison with other determinations. The data as a whole can be expressed in terms of wave-length and temperature, assuming Benoit's linear thermal expansion formula $\perp$ to the axis, as follows:[12]

$$10^3\ (N_\epsilon - N_\omega)_t = 8.860\ 27 + \frac{0.107\ 85}{\lambda^2} + \frac{0.002\ 136}{\lambda^4} - 0.166\ 67\ \lambda^2$$

$$- 10^{-3}\, t \left(1 + \frac{t}{900}\right)(1.01 + 0.2\lambda^2)$$

in which $(N_\epsilon - N_\omega)_t$ is the birefringence at centigrade temperature t, and λ is the wave-length, in μ, in air at 15°.

TABLE XXXII.3.

BIREFRINGENCE OF QUARTZ, IN AIR AT SAME TEMPERATURE. MACÉ DE LÉPINAY, 1891.

Radiation solar line	Wave-length mμ	$10^3\ (N_\epsilon - N_\omega)$	
		$t = 0°$	$t = 18°$
S	310.03	10.176 4	10.157 7
r	314.37	10.135 2	10.116 5
Q	328.675	10.007 0	9.988 3
P	336.118	9.947 3	9.928 5
O	344.08	9.889 4	9.870 6
N	358 120	9.797 4	9.778 6
M	372.76	9.714 1	9.695 2
L	382.043	9.665 6	9.646 7
H′	395.29	9.604 2	9.585 3
h (Hδ)	410.174	9.541 6	9.522 7
G	430.79	9.467 1	9.448 0
F	486.133	9.312 1	9.292 8
b_1	518.362	9.243 9	9.224 5
D	589.29	9.129 0	9.109 3
C	656.278	9.049 3	9.029 3
B_1	688.38	9.017 7	8.997 5

The birefringence of quartz for mercury green light (546.072) was determined with high precision by Macé de Lépinay[13] in 1900, using Dongier's method. Readings were made at 7 temperatures between 12 and 27°C. The results are stated by the following expression, which I have recalculated in altered form to make it comparable with other data:

$$10^6\ (N_\epsilon - N_\omega) = 9\,193.71 - 1.029\,t - 0.002\,3\,t^2$$

The value is a little lower than that interpolated from the 1891 series, but is within the limits of error of the earlier method.

[12] The formula contains the original temperature terms, with wave-length terms as revised in 1900 (MACÉ, article cited in XXXIII, note [16]).

[13] Article cited in XXXIII, note [16].

Ehringhaus [14] has developed a method for measuring the birefringence relatively to a known value of this constant at some one frequency. Even though

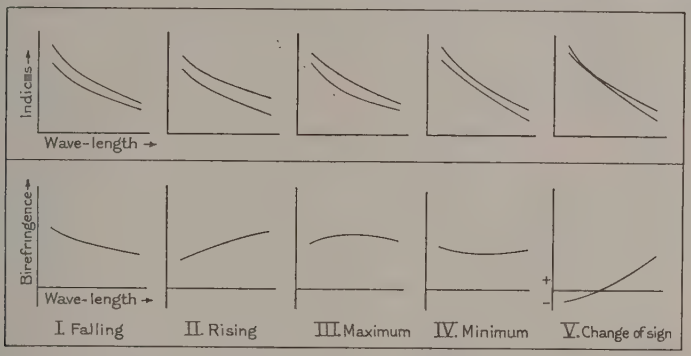


FIG. XXXII.2.—Types of dispersion of the birefringence of uniaxial substances. (Ehringhaus.)

this one value is not known accurately, the method still shows the character of the dispersion of the birefringence. The method depends upon a spectral analy-

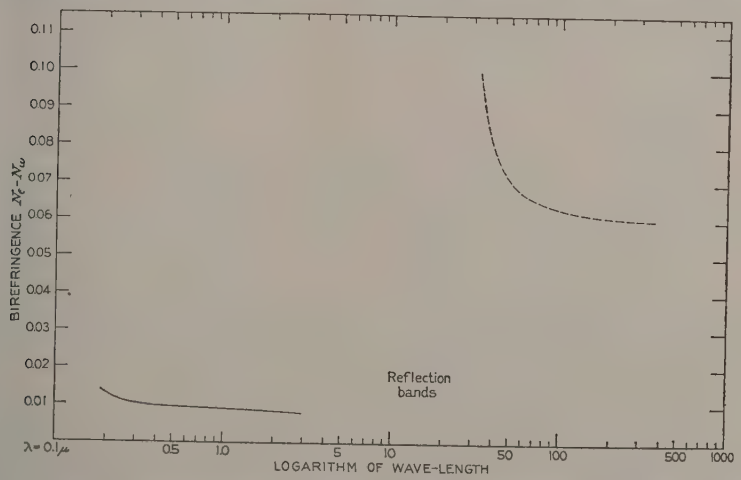


FIG. XXXII.3.—Birefringence of quartz at room temperature, as related to the frequency.

sis of the interference colors produced when plane-polarized white light is sent through a plane-parallel plate of the substance.

[14] EHRINGHAUS, A., Neu. Jahrb. Min. (1917) Beil.-Bd. 41: 342-419.

Ehringhaus measured the birefringence of quartz by the above-described method at 37 wave-lengths between 758 and 405 mμ, at 18.6°C. The curve of birefringence so obtained coincides within 20×10^{-6} with the curve deduced from Gifford's precise index measurements (p. 617).

The values of birefringence deduced from Carvallo's measurements of N_ϵ and N_ω between 599 and 2172 mμ are in close agreement with the formula of Macé de Lépinay (1891).

Dispersion of the birefringence

As remarked at p. 640, it is customary to refer to the general manner of variation of a refractive index with the frequency as its "dispersion". Since the birefringence is only a difference between refractive indices, this constant, likewise, may be considered to have a dispersion.

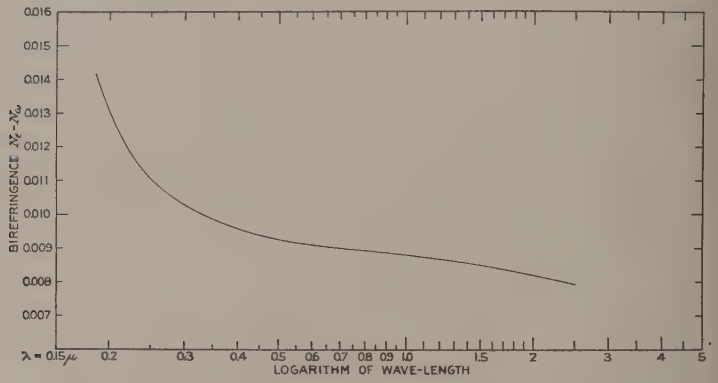


Fig. XXXII.4.—Birefringence of quartz at 18°, for visible and near ultra-violet and ultra-red radiation.

The different possible kinds of dispersion of the birefringence will be obvious from a consideration of the possible combinations of variations, and some of them are illustrated by the sketches in Figure XXXII.2. All of these different types of dispersion have been observed.

The dispersion of the birefringence of quartz is of type I, that is, the birefringence increases with the frequency, or falls as the wave-length increases from violet toward red. Another analogy between silica and water, in addition to those commented upon in earlier chapters, is seen in the fact that ice also has a birefringence-frequency curve of type I.

Figure XXXII.3 presents a general view of the birefringence of quartz at room temperatures. The curve for the farther ultra-red is not very certain, based as it is upon the differences between indices which have been obtained only by calculation from reflecting power.

Figure XXXII.4 gives the accurately known part of the curve on a larger scale.

Relative dispersion of birefringence

By analogy with the relative dispersion of the refractive index we can define a *relative dispersion of the birefringence,* D_B, by the formula

$$\frac{1}{D_B} = \frac{B_F - B_C}{B_D}$$

in which B_F, B_C, and B_D are the values of the birefringence at solar lines F, C, and D, respectively.

Some experimental values of D_B for quartz at room temperature are:

Macé	34.6
Ehringhaus	33.7
Table XXX.2	34.2
Gifford	33.6

In other words, if the frequency is increased from that of line C to that of line F the birefringence increases by about one thirty-fourth of the value which it has at the intermediate line D.

This is practically the same as the relative dispersion of the birefringence of ice (34.2).

Nothing whatever is known of the dispersion of the birefringence of tridymite and cristobalite.

Chapter XXXIII. ROTATORY POWER

As already noted, quartz belongs in the class of "birefringent uniaxial substances" whose general characteristics have been described (p. 587); but with a difference. It belongs to a special class consisting of substances which, instead of transmitting two *plane*-polarized rays, cause the light of both rays to become *elliptically*-polarized. In certain directions these elliptically-polarized rays may (but do not necessarily) reduce to plane-polarized or to circularly-polarized rays.

Such substances are called "optically active" or *optically rotatory,* for reasons now to be given.

Light traveling through quartz in the direction of the principal crystallographic axis, which is also the optic axis, may be looked upon as progressing in the form of two circularly-polarized waves of opposite sign, and of slightly different speed. In a non-rotatory uniaxial substance these two rays, the ordinary and extraordinary, would have the same velocity parallel to the axis. In quartz and other rotatory substances the velocities are not the same. The difference is very small, usually much less than the difference between the maximum and minimum of the extraordinary ray, but the difference is still large enough so that when the two sets of waves recombine on emerging from the crystal to form a plane-polarized wave, the plane of polarization is found to have been rotated away from its original position.

The angle of this rotation, per mm thickness of the substance, is called the *rotatory power* of the substance. It will be indicated in this book by the symbol ρ.

Quantitative statement of rotatory power

In the most general case the statement of rotatory power for a given frequency and temperature requires 9 constants. These are reduced in number, as with the 21 elastic constants, by considerations of symmetry. Thus for the trigonal trapezohedral and hexagonal trapezohedral classes, to which belong low-quartz and high-quartz, respectively, the 9 constants are reduced to 2. One of these applies to the principal axis, and is called the *principal rotatory power.* It is the one which is commonly measured.

The other constant applies to directions perpendicular to the axis, because quartz does not transmit two perfectly-plane-polarized waves in a direction perpendicular to the axis, but two very slightly elliptically-polarized waves.

The principal rotatory power of quartz is logically derivable from the two refractive indices of quartz for right-rotating and left-rotating circularly-polarized radiation parallel to the optic axis. Being thus similar in character to an index of refraction, the rotatory power may vary with

the frequency (wave-length) of the radiation, the temperature, and the pressure or stress, and in general with any variable which influences the shape, arrangement, or distance apart of the atoms.

The rotatory power of quartz

The phenomena actually observed in quartz are these:

(a) If a plate be cut from a quartz crystal perpendicular to the principal axis, and if plane-polarized monochromatic light be sent perpendicularly through the plate, the plane of polarization is found to have been rotated by the quartz.

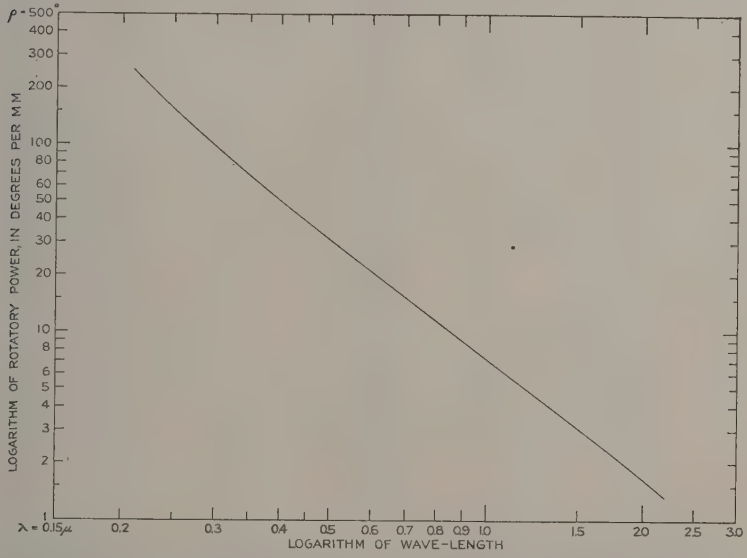


Fig. XXXII.1.—Relation between the rotatory power of quartz at room temperature and the wave-length. (Note that the scales of both coordinates are logarithmic.)

(b) The angle of rotation is proportional to the thickness of the plate.

(c) The rotation is opposite in direction, but equal in amount, in the two crystallographically different varieties known as right-quartz and left-quartz (see p. 188). By convention of names, right-quartz produces clockwise (right) rotation, and left-quartz produces counter-clockwise (left) rotation, as viewed by an observer toward whom the light is coming. With reference to their rotatory power, these two kinds will be called *dextro-quartz* and *levo-quartz*.

Table XXXIII.1 contains the most probable values of the rotatory power of quartz for a series of frequencies, at room temperature. The wave-lengths are consistent with those used in Chapter XXX and elsewhere. The relation of rotatory power and frequency is shown graphically in Figure XXXIII.1.

TABLE XXXIII.1.

MOST PROBABLE VALUES OF THE ROTATORY POWER OF QUARTZ AT VARIOUS FREQUENCIES, AT 20° C.

Radiating element	Wave-length in air at 15° mμ	ρ Degrees per mm
Cd	226.503	201.9
Cd	231.288	190.5
Au	242.796	166.9
Au	250.329	153.9
Cd	274.867	121.10
Sn	303.412	95.02
Cd	340.365	72.45
Fe	348.534	68.585
Ca	396.848	51.115
Hg	404.656	48.945
H	410.174	47.495
H	434.047	41.924
Hg	435.834	41.548
Cd	467.815	35.601
H ("F")	486.133	32.761
Cd	508.582	29.728
Hg	546.072	25.535
Na (mean)	589.29	21.724
Cd	643.847	18.023
Li	670.786	16.535
He	728.135	13.924
Rb	794.763	11.589
Hg	1014.06	6.976
...	1200.00	4.889
Hg	1529.61	2.930
He	2058.20	1.527
...	2500.00	0.972

The rotatory power of quartz which has been selected and tested optically with very great care is constant within 0.008 degree per mm in sodium light, or about 0.04 per cent. If the specimens have not been carefully tested, even though they may appear to be free from twinning or other flaws, the rotatory power may vary by two or three times as much.

Note on the nomenclature of rotatory power

The naming of "right" and "left" rotations of the plane of polarization is wholly a matter of convention, about which some confusion has arisen. It is so closely associated with the early work on quartz that a note on the subject will not be out of place here.

Biot,[1] while studying the phenomena produced by plane-polarized white

[1] BIOT, *Mémoire sur un nouveau genre d'oscillation,* etc., Mem. Cl. Sci. Math. et Phys., Inst. Imp. France 1812, I: 1-371 (1814), especially pp. 241-243.

light which had been passed through a crystal plate and then analyzed by means of a rhomb of calcite, discovered in 1813 that there are two kinds of quartz, which, so far as he could discern, were exactly alike in external appearance yet gave different optical effects. One of the two, he found, gives the same succession of colors in the *extraordinary* ray as are seen in Newton's rings by reflected light, counting toward the center (*"ascending"* order), when the analyzing calcite rhomb is turned *clockwise* by the observer, who is looking through it *toward* the light-source. The second kind of quartz gives the opposite succession of colors when all conditions remain the same and the rhomb is also turned clockwise as before.

Biot referred to the first kind as "rotating the light from left to right," illustrating this phrase by means of an arrow indicating the direction which we now commonly call "clockwise," and showed that such a deviation of a part of the "luminous molecules" would account for the phenomena.

If instead of looking into the analyzer, with the light coming toward him, the observer imagines himself traveling with the light, Biot's clockwise rotation will appear counter-clockwise, or left-handed. Herschel[2] in 1820 proposed that a quartz crystal showing this kind of rotation be named a "left-handed crystal," and, by association, gave the same name to the rotation itself. Herschel's convention as to the direction from which the rotation is to be viewed seems the more objective and logical, but Biot's was the first proposed; and it has therefore, very properly, been adopted in most text-books, and will be adhered to in this book. Although Biot himself did not name a given rotation either right or left, but always used an arrow to indicate the direction, his point of view is the one adopted when we speak of right, right-handed, or clockwise rotation.

The naming of right-handed and left-handed *crystals* is a geometrical convention quite independent of the naming of right and left rotation of the polarization-plane. It happens that the kind of quartz crystal now universally known as right-quartz rotates the plane to the right or clockwise, in the Biot sense, but rotates it counter-clockwise in the Herschel sense.[3]

Rotatory power in other forms of silica

There is no reason in the general theory of optical rotation why rotatory power might not be found in any of the other modifications of silica as well as in quartz. Even vitreous silica would not be excluded, for there are many rotatory liquids, solutions, and even gases.

Practically all the experimental work has been on low-quartz and high-quartz, and on vitreous silica. Available crystals of tridymite and cristobalite have been so small that no measurements have been attempted on those modifications.

Vitreous silica shows no observable rotatory power even with the most sensitive apparatus.

[2] Herschel, J. F. W., *On the rotation impressed by plates of rock crystal on the planes of polarization of the rays of light, as connected with certain peculiarities in its crystallization*, Trans. Cambridge Phil. Soc. (1821) 1: 43-52.

[3] Dana's *Text-book* and Dana's *Manual* use the Herschel convention, but the statement of its relation to right- and left-handed substances is inconsistent.

The experimental data on rotatory power

Constancy of the rotatory power of quartz

Lowry's experiments

Lowry's measurements of rotatory power[4] furnish some of the most enlightening information that we have on the problem of the constancy of the properties of quartz.

Plates were first selected which passed the test with polarized light as usually applied (see p. 835). Readings of rotatory power on 20 such specimens, each about 25 mm in thickness, then served to eliminate 8 of the 20, either because striae were revealed by the monochromatic (mercury green) light or because the readings varied measurably when the plates were rotated.

The remaining 12 consisted of 5 *levo*-rotatory[5] and 7 *dextro*-rotatory[5] specimens. These were cemented into two groups, one dextro-rotatory, one levo-rotatory. It was then found that there was a slight difference in setting according as the half-shadow angle was thrown to the left or right, and the mean was therefore taken. A new set of measurements yielded the following mean values for ρ for the green mercury line, $\lambda = 546.072$:

Specimens	Total rotation Degrees	ρ at 20° Degrees per mm
7 dextro-cylinders	4481.57	25.5338
5 levo-cylinders	3136.47	25.5338

Although the agreement seemed perfect, nevertheless when a new series was made, with the cylinders simply in optical contact but placed in varying positions, the differences between right and left half-shadow angles was quite variable, and the means also differed a little from the previous set:

7 dextro-cylinders	4481.76
5 levo-cylinders	3136.53

These variations were finally traced to flaws, evidently due to twinning, which had not been revealed by any previous tests but became evident when the half-shadow angle was set at zero and the eyepiece was drawn out of the telescope of the polarimeter so that it was possible to focus upon the interior of the specimens. In mercury green light a series of black and green bands was thus revealed, in 10 out of the 12 good plates, some of the specimens showing two series of bands inclined to one another.

Application was then made of this sensitive test to additional specimens of quartz, some of which, though guaranteed by an optical manufacturer to be perfect after being tested in the most stringent way known to him, yet failed to pass. 12 specimens were finally obtained (8 dextro- and 4 levo-quartz)

[4] Lowry, T. M., *The natural and magnetic rotatory dispersion in quartz in the visible region of the spectrum*, Phil. Trans. Roy. Soc. Lond. (1912) A, **212**: 261-297.

[5] These are oppositely named by the author, but he is using the Herschel convention (see p. 649) according to his footnote (p. 263 of article cited).

which satisfied the following specifications: (1) No flaw or irregularity when viewed between crossed Nicols with monochromatic green light; (2) no differences in rotatory power when read with positive and negative half-shadow angles; (3) no differences in rotatory power greater than 0.001 degree per mm when the specimen is rotated about its axis.

With these specimens the following final mean values of ρ per mm at 20° were obtained:

	Dextro-quartz	Levo-quartz
As originally measured	25.5369	25.5361
Reground and cemented, first grouping	25.5371	25.5363
Reground and cemented, second grouping	25.5373	25.5360
General means	25.5371	25.5361

When measured singly the extreme variation in rotatory power for the 8 individual dextro-cylinders was only 0.0006 per mm.

The difference of 0.0010 degree between the dextro- and levo-quartz is real, but it does not seem likely that it is a difference which would be duplicated in other dextro- and levo-specimens of apparently equally good quality. This conclusion is based on the fact that the levo-quartz specimens above described were selected with some difficulty from the only sound portions of a block which was generally faulty, while the dextro-quartz was cut from a block which was of unusually good and uniform quality.

The extreme range in the foregoing series, between the poorest specimens which passed the ordinary tests for optical quality and the best of the specimens, is 0.0033 degree per mm, or 0.013 per cent.

Gumlich's comparisons

A careful comparison of various specimens of quartz was made by Gumlich,[6] using sodium light. The planeness and parallelism of the faces and their declination from exact perpendicularity to the optic axis were examined in each case. Measurements were made at room temperature, which varied between 14 and 26°C, and the results were corrected to 20° by an independently determined coefficient. The precision is about 0.002 degree.

The summarized results are as follows:

Source	Number of plates	Thickness mm	ρ at 20°
Brazil	8	1.2 to 10.5	21.7182 ± 0.0005
Switzerland	1	8.2	21.7225
Japan	1	8.3	21.7260

The differences are not larger than the possible error in the absolute value, when the errors due to position of axis, variability of thickness, and variability

[6] GUMLICH, E., *Optisches Drehungsvermögen des Quarzes für Natriumlicht*, Wiss. Abh. Phys.-Techn. Reichsanst. (1895) **2**: 201-256; Zeitschr. Instrumentenk. (1896) **16**: 97-115.

of temperature are taken into account. This was shown in part by the results of a further comparison in which 12 Brazilian plates, including 7 of those in the above table, were measured after being set up by their surfaces alone without regard to the position of the optic axis; they yielded the average value 21.7223 ± 0.0010.

The Reichsanstalt records

Schönrock[7] reported in 1901 that the 100-degree Ventzke plates tested in the Physikalisch-technische Reichsanstalt up to that date showed differences in the rotatory power per mm covering a range of 0.019 degree for sodium light, at 21.7°C. This is 0.087 per cent of the rotation. He estimated that the most unfavorable possible combination of errors could have yielded a difference of only 0.044 per cent. A real difference in this series of specimens evidently existed, but the important question is whether such a difference would still persist if all the plates were to be tested as rigorously as those studied by Gumlich, and the imperfect ones were to be left out. The plates tested by the Reichsanstalt were commercial products sent in by various manufacturers, and although they must have been of high optical quality there is little doubt that if all were brought together in one place and subjected to a rigorous selection some would not pass; the remainder might well be as constant in rotatory power as Lowry's and Gumlich's specimens. On the other hand, Schönrock's series probably represents a wider range of sources of quartz than would be available to any individual investigator. The problem of variability within a range of 0.04 per cent must therefore be left open. (See p. 25.)

Other data on constancy

Schönrock[8] has called attention to the discrepancy between the values of Gumlich and of Macé de Lépinay for mercury green light at 20°, which he believes to be greater than the experimental error. (See Table XXXIII.3.)

Buisson[9] found the rotatory power of quartz to differ slightly between the two standard cubes, both dextro-rotatory, which were used for the density comparisons already referred to (XVIII). The rotatory power for green mercury light, at 10°C, was:

4-cm cube, C_4	25.5025	degrees per mm
5-cm cube, C_5	25.5012	" " "
Difference	0.0013	" " "

The precision is not stated. According to the experience of Schönrock[10] the rotatory power can not be determined closer than 0.003 degree (0.012 per cent) in such a case as this. It appears probable, nevertheless, that a real difference does exist between the two specimens, since the excess of rotatory power in C_4 is paralleled by an excess in density, dilatation coefficient at 0°, and indices of refraction. (See pp. 292, 372, 605.)

Soret & Sarasin's[11] principal two specimens (30 and 60 mm thick) ap-

[7] Schönrock, Zeitschr. Instrumentenk. (1901) **21**: 150.
[8] Schönrock, place just cited.
[9] Buisson, article cited in XX, note [4].
[10] Schönrock, Zeitschr. Instrumentenk. (1907) **27**: 24-25.
[11] Article cited in note [22].

peared to show systematic differences in rotatory power in sodium light and in the ultra-violet, the 60-mm specimen being a little the lower. This was further tested by means of direct comparison by the method of Laurent's saccharimeter, which is capable of higher precision for such a comparison than the methods used for the direct measurements of rotatory power. The results are given in Table XXXIII.2.

TABLE XXXIII.2.

SORET & SARASIN'S COMPARISONS.

Specimen	Temp. of measurement	ρ per mm at 20°	Means
30-mm quartz (No. 2)	20.9	21.7278	
	19.48	21.7310	21.7296
	20.08	21.7300	
60-mm quartz (No. 4)	16.72	21.7107	
	21.2	21.7142	
	19.56	21.7141	21.7132
	20.07	21.7138	
Difference			0.0164

These results seemed to confirm the existence of a real difference, but the authors point out that if there is a difference of 0.0164 degree with sodium light, there should be a difference of 0.16 degree in the farthest ultra-violet, while the differences actually observed were about 0.04 degree. They conclude, therefore, that the apparent differences may be traceable to concealed errors.

CONSTANCY OF ROTATORY DISPERSION

The discussion so far has been only of the constancy of rotatory power for a single frequency. The constancy of the dispersion of the rotatory power is also of interest.

On this point we again have valuable information from Lowry's extensive measurements. Several complete series of determinations of rotatory power for all of his available visible frequencies were made on the specimens which had passed all usual tests for quality, but which were afterwards rejected as imperfect (see p. 650). The ratios of rotatory power at the extreme red (lithium) and violet (mercury) to that at the standard mercury green are shown below, compared with similar ratios for the best levo- and dextro-quartz specimens finally accepted.

Specimens	$\frac{\rho\ (\text{Li})}{\rho\ (\text{Hg green})}$	$\frac{\rho\ (\text{Hg violet})}{\rho\ (\text{Hg green})}$
Best dextro-quartz	0.647 539	1.626 987
Best levo-quartz	0.647 508	1.627 001
Earlier set, afterwards rejected	0.647 589	1.626 753
(Earlier set) — (average of best)	+ 0.000 064	— 0.000 241

The differences between the best levo- and dextro-quartz are within the possible errors of measurement. Furthermore, the ratios for other frequencies

show no drift with the frequency. On the other hand, the differences between the average of the best specimens and the earlier unsatisfactory specimens are consistently positive towards the red and negative towards the violet. The differences are such as would be produced by admixture of a substance having a similar law of dispersion to quartz, but having a lower dispersive power.

Comparison of results at a single frequency

Sodium lines

The only spectrum line which is common to any considerable number of determinations of rotatory power by different investigators is the yellow sodium line.

The choice of sodium light as a standard for so much of the earlier work of precision in optical physics was unfortunate, because the "line" is double and the two parts differ in brightness. This would not necessarily be troublesome, were it not for the fact that the relative width and brightness of the two parts vary with conditions. Hence the so-called "optical center of gravity" of sodium light is not a constant wave-length.

Table XXXIII.3.

Rotatory Power of Quartz at 20° C for the Optical Center of Gravity of Sodium Light, About 589.3 mμ.

Observer	Source of light	λ mμ	ρ Degrees per mm
Lang (1876)	Sunlight	589.3	21.724
Soret & Sarasin (1882)	Sunlight	589.3	21.708
Soret & Guye (1893)	NaBr flame, purified	589.3	21.723 †
Gumlich (1896)	Sodium flame, purified	589.3	21.724 †
Schönrock * (1898)	Sodium flame, purified	589.3	21.722
Lowry (1912)	Na glass in carbon arc	589.26	21.728

* Schönrock, O., pp. 373-374 of Landolt: *Das optische Drehungsvermögen*, etc., 1898.

† Corrected by Schönrock to wave-length 589.3 (p. 373 of Landolt, cited above).

Gumlich [12] could find no definite effect of the temperature of his sodium flame on the measured rotatory power of quartz, but Zöllner, Ebert, and Schönrock have all found that the optical center of gravity is shifted towards the red when the brightness is increased. This was again confirmed by Lowry,[13] who found that the rotatory power of quartz as measured in sodium light was decreased by 0.007 per cent (0.04 degree in 562.8 degrees) when an oxygen-jet was used in the sodium flame. The center of gravity may not always be as variable, however, as might appear from these statements. Bates,[14] whose work has been largely responsible for displacing the unsatisfactory sodium light by better monochromatic sources, showed that the lines produced by a rod of

[12] Gumlich, E., article cited in note [6].

[13] Article cited.

[14] Bates, F., Bull. Bur. Standards (1906) **2**: 239-248 (Sci. Paper 34).

sodium carbonate in different positions in an oxy-hydrogen flame are constant in wave-length to well within 0.5 mμ, though differing in width.

In general, it appears that the center of gravity, which is at about 589.25 mμ, is subject under ordinary conditions to changes of the order of 0.1 mμ, corresponding to about 0.007 degree in the rotatory power of quartz.

Lowry also confirmed the observation of Zöllner that the line D_2 widens symmetrically with increasing brightness while D_1 widens more rapidly toward the red side. Readings on D_2 are therefore more reproducible than readings on D_1.

Omitting several results of lower accuracy, Table XXXIII.3 contains a comparison of the best measurements of the rotatory power of quartz for sodium light. References to the original data will be found elsewhere in this chapter.

Green mercury line

Comparisons are also possible of several measurements at the green mercury line, $\lambda = 546.072$ mμ. This is a much more reproducible frequency than the sodium yellow.[15] The results are given in Table XXXIII.4.

The measurement by Macé de Lépinay[16] was made on the standard cube C_4 which has several times been referred to (XVIII and XXXI), using his newly described "analyseur à pénombres." From the mean values of 4 experiments at each of the temperatures 13.40 and 19.43°, the final result for the rotatory power of a plate having a thickness of 1 mm at 0° (after correcting an obvious mistake in the published coefficient) is:

$$\rho = 25.5171 + 0.0046\ (t - 15)$$

TABLE XXXIII.4.

ROTATORY POWER OF QUARTZ AT 20° C FOR GREEN MERCURY LIGHT, $\lambda = 546.072$ mμ.

Observer	Date	ρ
Gumlich	1898	25.5317
Macé de Lépinay *	1900	25.5365
Lowry	1912	25.5371

* As recalculated by SCHÖNROCK, Zeitschr. Instrumentenk. (1901) **21**: 90-92.

Ratios

A further comparison is possible by taking the ratio between the rotations at the sodium and mercury lines.

This ratio has been carefully measured by Bates,[17] who used 5 plates whose sodium rotation had been measured at the German Reichsanstalt. Their rotation was measured again by Bates himself at the U. S. Bureau of Standards, and the mean of the two sets was taken as the basis of comparison. The values of the ratio $\rho_{546.1} : \rho_{589.25}$ all fell between 1.175 19 and 1.175 12, with a mean of 1.175 17. This result is further compared with other available ratios in Table XXXIII.5.

[15] See Bates, article cited (1906).
[16] MACÉ DE LÉPINAY, J., Journ. de Physique (1900) (3) **9**: 644-652.
[17] BATES, F., article cited.

TABLE XXXIII.5.

COMPARISONS OF RELATIVE ROTATORY POWER OF QUARTZ.

	Date	$\rho_{546.1}/\rho_{589.3}$
Bates	1906	1.175 17
Lowry	1912	1.175 29
Gumlich	1898	1.175 27

EXPERIMENTAL DATA ON THE RELATION OF ROTATORY POWER AND FREQUENCY IN QUARTZ

Visible and ultra-violet

The most extensive measurements of the rotatory power of quartz at room temperatures are those of Lowry, and Table XXXIII.1 is based primarily on his data. They cover a wide range of frequencies, from wave-length 0.233 μ in the ultra-violet to 1.7 μ in the ultra-red.

The data on 24 frequencies in the visible spectrum were published in 1912.[18] Measurements were also made at 700 frequencies in the ultra-violet, but have not been published in full. The values for 20 iron-arc lines from this series of 700 were published in 1923.[19] Reference was also made in 1923 to preliminary results of the measurements in the ultra-red, in connection with rotatory dispersion formulas (see p. 670).

For the visible spectrum Lowry used a combination of Perkin's and Lippich's methods. The distinguishing characteristic of Perkin's method is the employment of a direct-vision spectroscope in front of the eyepiece of a polarimeter; while Lippich's method consists in the resolution of the light by a spectroscope before it enters the polarizer. The series of parts in the apparatus thus consisted of: (1) the source of light, either flame or arc; (2) a condenser; (3) a collimator, constant-deviation prism, and eyepiece tube, constituting together a constant-deviation spectroscope; (4) the polarizer, of the triple-field type; (5) the quartz specimen, in a water-jacketed tube to preserve constant temperature; (6) the analyzer, graduated circle, and eyepiece; (7) an ordinary direct-vision prism or a Rutherford prism, serving for the final resolution of the light. By various means the dispersive power of this system was increased until in its final form the separation of the two lines of the yellow mercury pair, 576.9 and 579.0 mμ, was 1.85 mm.

The readings, consisting of the actual rotations of both dextro- and levo-quartz and also of the net rotations produced by a combination of 226 mm of dextro-quartz[20] with 181 mm of levo-quartz,[20] were all computed in the form of ratios between the rotatory power at the given wave-length and the rotatory power for mercury green, taken as 25.5371 degrees per mm (see p. 651).

The relative precision attained in these measurements seems to be very high, but the apparent increase in accuracy obtained by using such an unusually long specimen of quartz may be illusory. It is like using a 20-gram sample

[18] LOWRY, T. M., article cited.

[19] LOWRY, T. M., *Glazebrook's Dictionary Applied Physics* (London, 1923) Vol. 4, pp. 537-541.

[20] See note [5].

for a chemical analysis, or a thermometer with a 10-cc bulb; some of the errors are relative, not absolute, and are little influenced by the size of the

TABLE XXXIII.6.

MEASUREMENTS OF ROTATORY POWER, PER MM, OF QUARTZ, AT 20° C.

Source	Wave-length mμ	ρ (Lowry)	ρ (Gumlich)
Fe	232.739	187.225	
Fe	241.331	169.661	
Fe	267.906	129.200	
Fe	281.329	114.277	
Fe	294.135	102.434	
Fe	312.566	88.483	
Fe	332.374	76.551	
Fe	348.534	68.586	
Fe	364.039	62.085	
Fe	380.535	56.163	
Fe	393.582	52.066	
Hg	404.656		48.9297
Fe	411.855	47.068	
Fe	423.361	44.289	
Hg	435.834	41.5487	41.5478
Fe	437.593	41.183	
Fe	453.115	38.162	
Fe	464.744	36.114	
Cd 6	467.815	35.6043	
Zn	468.014	35.5712	
Zn	472.216	34.8875	
Fe	478.966	33.830	
Cd 5	479.991	33.6761	33.6673
Zn	481.053	33.5154	
Hg	491.60		31.9667
Fe	500.187	30.813	
Cd 4	508.582	29.7308	29.7238
Cu	510.555	29.4851	
Cu	515.324	28.9036	
Ag	520.904	28.2447	
Fe	523.295	27.966	
Tl	535.047	26.6718	
Fe	537.149	26.448	
Hg	546.072	25.5371	25.5317
Ag	546.543	25.4911	
Ag	547.151	25.4318	
Cu	570.025	23.3101	
Hg	576.960	22.7201	22.7184
Cu	578.213	22.6157	
Hg	579.066	22.5455	22.5465
Na	588.997	21.7483	
Na (center)	589.26	21.7283	21.720
Na	589.593	21.7001	
Zn	636.235	18.4786	
Cd 1	643.847	18.0225	
H	656.278		17.3126
Li	670.786	16.5359	16.5347

sample. Quartz is never quite homogeneous, and always scatters some light (see XXXVIII), and it may be questioned whether the accuracy is any greater for a 20-cm than for a 1-cm path.

The published data are given in Table XXXIII.6, with wave-lengths altered to recent accepted values consistent with other chapters of this book (see p. 590).

Gumlich [21] made a series of careful measurements on the rotatory power of quartz at 10 visible frequencies, using the mercury arc, hydrogen tube, and lithium flame as sources. He employed Lippich's method of a dispersing prism

TABLE XXXIII.7.

ROTATORY POWER OF QUARTZ AT 20° C, AS MEASURED BY SORET & SARASIN (1882).

Radiation	Wave-length mμ	ρ per mm	
		No. 2	No. 4
Cd 26	214.439	235.972	.....
Cd 25	219.462	220.731	220.691
Cd 24	226.503	201.824	201.770
*Cd 23	231.288	190.426	.....
Cd 18	257.304	143.266	143.229
Cd 17	274.867	121.052	121.063
*R	318.0	84.972	84.991
*Cd 12 [?]	324.70[?]	80.459	.....
Q solar	328.68	78.579	78.598
P solar	336.12	74.751	74.592
Cd 11	340.365	72.448	.....
O solar	344.10	70.587	70.588
Cd 10	346.69	69.454	.....
*N solar	358.12	64.459	.....
*Cd 9	361.25	63.268	63.229
M solar	372.76	58.894	58.876
*L solar	382.04	55.625	.....
*K solar	393.367	52.155	.....
*H solar	396.848	51.193	51.182
h(Hδ) solar	410.174	47.481	47.492
*G solar	430.79	42.604	42.568
F solar	486.133	32.773	32.749
E solar	526.99	27.543	27.537
D_3 solar	588.997	21.727	21.724
D_1 solar	589.593	21.684	21.696
C solar	656.278	17.318	17.307
B solar	687.2	15.746	.....
a solar	718.9	14.304	14.298
*A solar	760.7	12.668	12.628

* The measurements at these frequencies are less exact because the lines are not well adapted to precise observation.

preceding the analyzer, with Lummer's half-shadow device of a total-reflecting prism with strips of silvering. Four plates were used, three of which were from Brazil and one from Switzerland; thicknesses 3.4 to 24.1 mm. No systematic differences between specimens were observed (see p. 651). Measurements were made at room temperature, and were recalculated to 20°.

The results, including also an earlier determination by Gumlich,[22] on the sodium line, are included in Table XXXIII.6. The precision is about 0.002 degree.

[21] GUMLICH, E., *Rotationsdispersion und Temperaturcoefficient des Quarzes*, Ann. Phys. u. Chem. (Wiedemann) (1898) **64**: 333-359.

[22] GUMLICH, E., article cited in note [6].

The first investigators to extend accurate observations of the rotatory power of quartz into the ultra-violet spectrum were Soret & Sarasin.[23] This painstaking work, covering several years, consists of 6 series of measurements at 15 to 19 frequencies with sunlight as source; a second set of measurements with sodium light; and 3 series at 5 to 10 frequencies of the spark spectrum of cadmium. The precision is of the order of 0.005 to 0.05 degree, depending upon the light source, the frequency, and the method employed.

The summarized results are contained in Table XXXIII.7, with corrected wave-lengths (see p. 590). Three specimens of quartz were employed but most of the results were obtained with Nos. 2 and 4, having thicknesses of 30 and 60 mm, respectively.

Ultra-red

The most probable values of the rotatory power of quartz in the ultra-red spectrum are based upon the work of Dongier (1897) and Ingersoll (1917), supported by the earlier measurements of Carvallo, Hupe, Moreau, and Hussell.

A set of very careful and exact measurements was made by Dongier.[24] He used a method similar to that previously employed by Carvallo for the refractive indices of fluorite, namely, to identify the wave-lengths which give total rotations differing successively by 90 degrees. The spectrum of white radiation which has passed through a polarizer, a thickness of quartz, and an analyzer, contains alternate maxima and minima of intensity (light and dark bands). When the analyzer is turned 90 degrees, the maxima and minima interchange places. If a double-image analyzer is used, the two spectra are produced side by side, and the successive frequencies, 90 degrees apart, at which the intensities of the two spectra are exactly equal, can be identified with fair precision.

In Dongier's apparatus a carbon arc was used as the source of heat radiation, and a prism of calcite served both as polarizer and as dispersing prism for the production of monochromatic radiation. The results therefore depend upon a knowledge of the relation between the wave-length and the index of refraction of calcite at various wave-lengths. Carvallo's data on calcite were made the basis of the calculations.

Dongier's measurements were made at 9 frequencies between 0.761 and 2.4 μ. The first 8, extending to 1.74 μ, were made on a 61-mm thickness of quartz. The last, at 2.20 μ, was made on a thickness of 27 mm, and two Wollaston prisms in parallel were used as analyzer in order to avoid the error due to dichroism which begins to be appreciable beyond 2 μ (see p. 720).

The results first published[25] were later revised in accord with Carvallo's latest data on the refractive indices of calcite.[26] The revised data on quartz are given in Table XXXIII.8 and Figure XXXIII.3. The accidental errors in this method are in λ rather than in ρ, and the precision is about 0.003 μ in λ.

[23] Soret, J. L., & Sarasin, E., *Sur la polarisation rotatoire du quartz,* Arch. sci. phys. nat. (1882) (3) **8**: 5-59, 97-132, 201-229.

[24] Dongier, R., *Pouvoir rotatoire du quartz dans l'infra-rouge,* Thèses, Paris, 1898, pp. 1-61. Ann. Chim. et Phys. (1898) (7) **14**: 331-391.

[25] Dongier, Compt. rend. Ac. Sci. Paris (1897) **125**: 228-230.

[26] Carvallo, E., Compt. rend. (1898) **126**: 950-953.

TABLE XXXIII.8.

ROTATORY POWER OF QUARTZ IN THE ULTRA-RED AT 18° C, AS MEASURED BY DONGIER.

Wave-length μ	ρ Degrees per mm
0.761	12.59
0.810	11.11
0.868	9.63
0.940	8.14
1.035	6.66
1.170	5.18
1.369	3.70
1.744	2.22
2.20	1.66

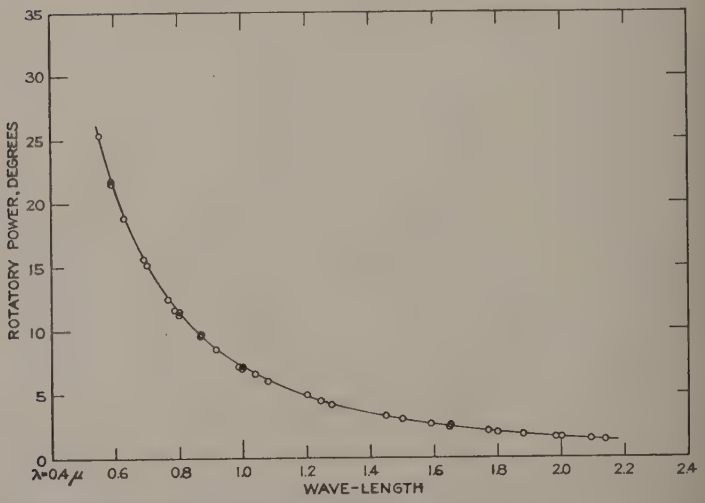


FIG. XXXIII.2.—Experimental data on the rotatory power of quartz for ultra-red radiation. Data of Ingersoll, 1917.

The most recent determinations of the rotatory power of quartz in the ultra-red are those of Ingersoll.[21] The method is an extension of that used for magneto-optic rotation (see p. 777), depending on the deflections of a differential bolometer when the two images delivered by a double-image analyzer are rendered unequal in intensity by the rotatory power of the substance. The zero reference condition in the magnetic measurement cannot be duplicated in the case of natural rotation, but a corresponding differential effect is obtained by turning the analyzer through exactly 90 degrees, thus interchanging the

[21] INGERSOLL, L. R., *Natural and magnetic rotatory dispersion in the infra-red spectrum,* Phys. Rev. (1917) (2) **9**: 257-268.

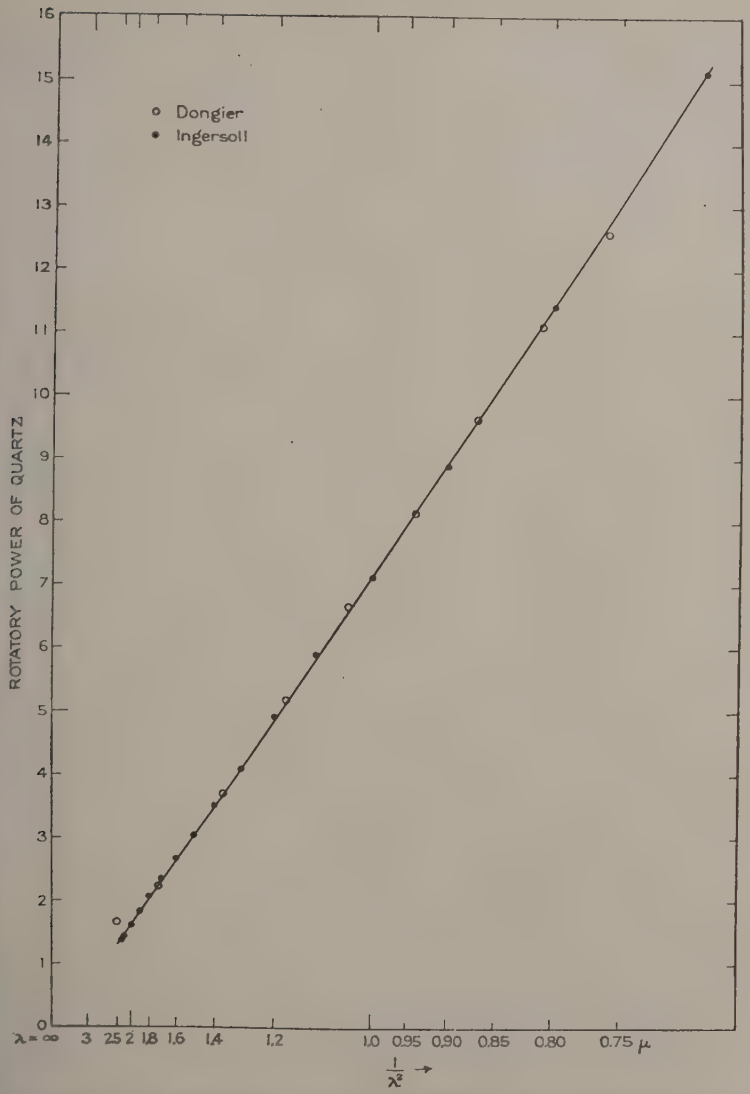


FIG. XXXIII.3.—A comparison of the data of Dongier (1897) and Ingersoll (1917) on the rotatory power of quartz for the ultra-red.

two rays and reversing the differential effect. The source was a lamp with a flat filament of tungsten.

Measurements of the natural rotation at 20°C were made at 24 frequencies between 0.5495 μ (visible) and 2.14 μ (ultra-red). The original data have not been published, but were shown in the form of a curve of rotations, which is copied in Figure XXXIII.2. The author's tabulated results, taken from the curve, are compared with Dongier's measurements in Figure XXXIII.3. The data are said to fit Lowry's formula (see p. 670) within the limits of error, less than 0.5 per cent.

Earlier measurements in the ultra-red

Of the data on the rotatory power of quartz in the ultra-red, measured before 1897, those of Carvallo come nearest to agreement with the most probable values. Those of Hussell are also in good agreement but do not extend beyond 1 μ. Hupe's values agree out to 1.6 μ but deviate considerably beyond that frequency. Moreau's values are almost certainly too low.

Hussell[28] measured the rotatory power at 6 frequencies, principally in the ultra-red, by a differential method employing the diverging interference bands which are produced when plane-polarized white light is passed through a Fresnel tri-prism of quartz and then through an analyzer and a dispersing prism. The bands in the ultra-red spectrum were recorded by means of Lommel's "phosphoro-graphic" method, which depends upon the fact that the ultra-red radiation concerned extinguishes the phosphorescence of certain phosphorescing powders, thus leaving both the interference bands and the Fraunhofer lines brighter than the intervening spaces. The value of the rotatory power for line A (12.668, Soret & Sarasin) was taken as the basis for the differential measurements.

Moreau[29] extended the range of precise measurement beyond Hussell's limit, to a wave-length of 1.715 μ. He employed the method of Desains. White radiation is passed through a polarizer, the plate of quartz to be tested, and an analyzer, and is then resolved into a spectrum by means of a prism. The intensity of the radiation coming out at a definite angle is measured in two positions of the analyzer at right angles to each other; from these two measurements the rotatory power is determined. The wave-length is known from the angle at which the radiation emerges, the goniometer which measures this angle having been previously calibrated in terms of wave-length.

Moreau used sunlight as source, and made 20 series of measurements at 9 frequencies between wave-lengths 0.842 and 1.715 μ.

The rotation of the analyzer through 90° is a possible source of error because it is likely to displace slightly the radiation, and this is particularly serious in Moreau's measurements because of the presence in solar radiation of strong absorption bands. Dongier believes this to be one of the principal reasons why Moreau's values fall below most of the others.

Carvallo[30] used a method very similar to Moreau's, just described, differing in that he made each pair of readings by turning the polarizer, instead of the

[28] Hussell, A., Ann. Physik u. Chem. (Wiedemann) (1891) **43**: 498-508.
[29] Moreau, G., Ann. Chim. et Phys. (1893) (6) **30**: 433-512.
[30] Carvallo, E., Ann. Chim. et Phys. (1892) (6) **26**: 113-144.

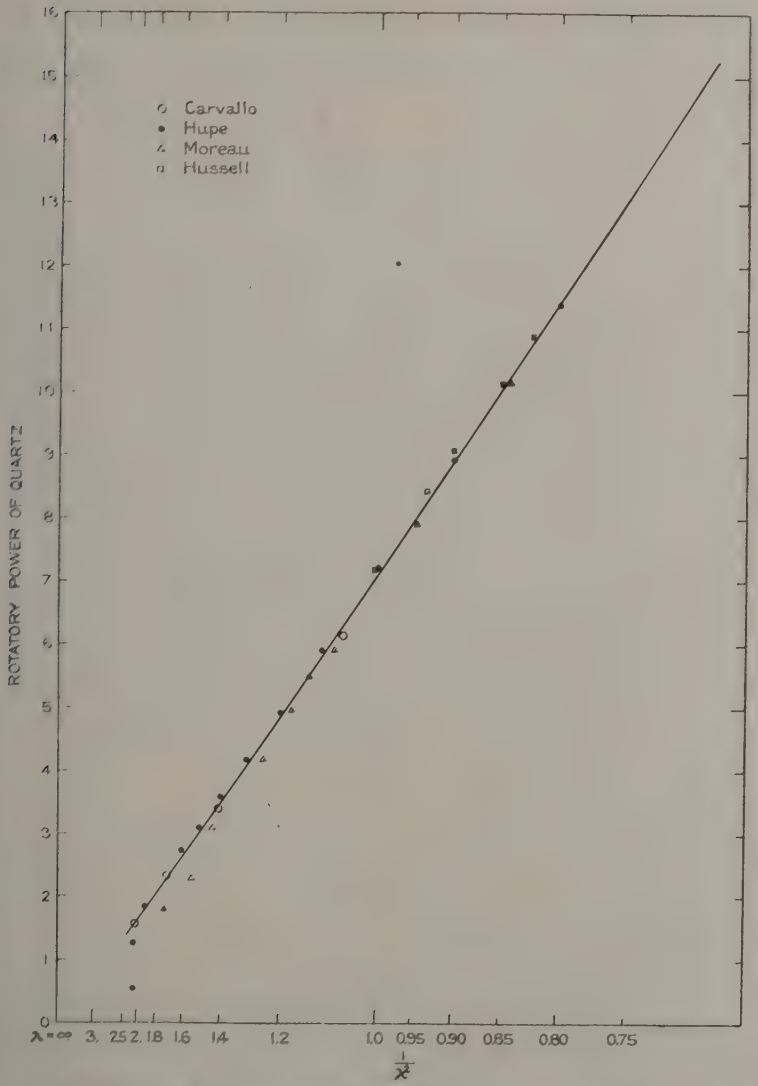


FIG. XXXIII.4. A comparison of some earlier measurements of the rotatory power of quartz for the ultra-red. The curve with which the points are to be compared is transferred from Figure XXXIII.3.

analyzer, through 90°. Carvallo used a Bourbouze burner as his source, and plates of quartz of thicknesses 7.4 and 8.2 mm. Measurements were made at 4 ultra-red frequencies. The results, as corrected by Dongier [31] to correspond with Carvallo's latest values for the refractive indices of calcite, are:

Wave-length, μ	ρ, degrees per mm
1.057	6.18
1.405	3.43
1.704	2.28
2.030	1.60

Dongier has called attention to the fact that the methods of both Moreau and Carvallo contained a possible source of error in a lens which was interposed between polarizer and quartz. The degree of isotropy or the state of strain of this lens was not known, and it may have contributed to the polarization phenomena enough effect of its own to account for the small deviation of Carvallo's from Dongier's results, but probably not enough to explain the much larger deviations of Moreau's results.

Hupe [32] measured the positions of the maxima and minima in the banded spectrum produced by a thickness of about 42 mm of dextro-quartz, using a Rubens bolometer. White radiation from a Linnemann zircon lamp was passed through a polarizer, collimator, flint-glass prism, the quartz plate, and an analyzer. The prism, previously calibrated, defined the wave-length. Dongier points out several sources of error in this method, principally (1) the effects of strain and of refraction in the glass lens and prism, which are added to the effect of the quartz, and (2) the uncertainty in determining the position of maxima and minima by the bolometer. The results do not seem very precise, since the accidental variations attain one-third of the quantity measured. The abnormal deviation at the longer wave-lengths is therefore probably due to concealed and accidental errors.

The measurements of Hupe, Carvallo, Moreau, and Hussell are plotted in Figure XXXIII.4 in comparison with the curve of Dongier's and Ingersoll's results, transferred from Figure XXXIII.3.

Historical notes on the rotatory power of quartz

Visible spectrum

So much of the pioneer work on optical rotation was done with quartz that a sketch of the early investigations on quartz is equivalent to a history of the growth of our knowledge of crystalline rotatory power in general.

The color effects due to the rotatory power of quartz were first observed by Arago [33] in 1811. He noticed that if a polarizer and an analyzer are crossed so that no light passes, and a plate of quartz is then placed between them, the quartz "depolarizes" the light in some way so that a part of it passes through the analyzer. At the same time, the light becomes colored.

[31] Dongier, R., p. 59 of thesis cited in note [24].
[32] Hupe, A., Wissenschaftliche Beilage, Progr. Realschule Charlottenburg (1894), 48 pp.
[33] Arago, Mem. Inst. de France, 1811, Pt. 1: 93-134.

Biot, in 1812, continued these experiments and arrived at the explanation now accepted.[24] The relation of rotatory power to frequency was studied in the succeeding years by Biot, who published in 1819 his law that "the rotations of the different simple rays are reciprocally proportional to the squares of their wave-lengths."

Following the very approximate measurements of Biot, a considerable improvement in method was made by Broch[25] (1846). He used sunlight as the source, passing it through a slit, a movable polarizer, the quartz plate, and an analyzer, the light then being resolved by means of a simple prism. By rotation of the polarizer a dark extinction band was made to coincide with each of the standard solar lines. The rotatory power was determined in this manner for the lines B, C, D, E, F, and G, on several specimens, part right-rotating and part left-rotating.

The use of artificial light was introduced by Stefan.[26] He also replaced Broch's single prism by a spectroscope, and measured the angles of refraction corresponding to rotations 180 degrees apart due to the quartz, as shown by successive extinction bands. Using thicknesses of quartz up to 70 mm, he established in this way a linear relation between the rotatory power of the quartz and the refractive indices of the spectroscope prism for varying frequencies. Independent measurements of the refraction of 7 solar lines by the same prism then made it possible to calculate the rotatory power of the quartz for each solar line.

Lang[27] improved upon Broch's method by using a double plate or column of quartz, consisting of a right-rotating and a left-rotating piece side by side. This produces two sets of bands which move in opposite directions when the polarizer is rotated, whereby the zero setting and the settings on the several solar lines can be made similar in character and therefore more precise. Lang obtained the following values with a 33-mm thickness of quartz:

Radiation	t	ρ, degrees per mm
C	21.9	17.299 ± 0.004
D	19.7	21.727 ± 0.003
F	21.4	32.722 ± 0.009

In his earlier work on the temperature coefficient of rotatory power Lang[28] measured the differences between lithium, sodium, and thallium light. Taking 21.728 degrees as the value for sodium light at 20° I have recalculated the other two:

Li	16.520
Tl	26.683

The precision of these is about 0.009 degree, and they agree well with the modern measurements in Table XXXIII.6.

[24] See note [1].
[25] Broch, Ann. Chim. et Phys. (1852) (3) **34**: 119-121.
[26] Stefan, J., Sitzungsb. K. Akad. Wiss. Wien, Math.-Nat. Cl. (1864) **50**, II: 88-124.
[27] Lang, V. von, Sitzungsb. K. Akad. Wiss. Wien, Math.-Nat. Cl. (1876) **74**, II: 209-214.
[28] Lang, V. von, Sitzungsb. K. Akad. Wiss. Wien, Math.-Nat. Cl. (1875) **71**, II: 707-714.

To improve the precision of reading small rotations Lippich introduced the spectroscope between the light source and the polarimeter. In the course of his subsequent experiments on half-shadow polarimetric apparatus Lippich [39] measured the rotatory power of a 1-mm plate of quartz under various conditions. The results are not of high absolute accuracy because of lack of parallelism of the faces, but agree with Lang's within the limit of accuracy.

In order to make the measurement of rotatory power at various frequencies convenient for the chemist, Landolt [40] replaced the spectroscope in Lippich's method by a set of filters, consisting of solutions of dyes or salts of definite concentration. He also used sodium light, purifying it of other visible radiations by means of potassium bichromate and uranous sulfate, as recommended by Lippich. Such purification is necessary if no spectroscope is used, as Landolt showed by comparing rotations measured with purified and with unpurified sodium light. The purified light gave rotations about 0.2 to 0.4 per cent lower than the unpurified.

Landolt's mean value for quartz, using purified sodium light, and 3 plates of thickness 0.5 to 2.5 mm, is 21.700, with a precision of about 0.03 degree.

Measurements of the rotatory power of quartz by Peddie,[41] by Wasastjerna,[42] and by Rose [43] are of lower precision, or for other reasons are not of independent value, and need not be further considered here.

Ultra-violet and ultra-red

A beginning of measurements of the rotatory power of quartz in the ultra-violet was made by Croullebois about 1870, but his results were not published until 1875,[44] when Soret & Sarasin [45] also published preliminary results. Croullebois' measurements were on solar lines H, L, M, N, and O, while Soret & Sarasin's extended from A, in the red, to N (see p. 658).

The first measurements of the rotatory power of quartz in the ultra-red were made by Desains [46] in 1866, using solar radiation. He repeated the measurements, using a lamp source, in 1877.[47] As the frequencies were known only very approximately, the results need not be considered in comparison with later more exact determinations.

The experimental data on rotation in vitreous silica

Biot,[48] interested as he was in the rotatory power of quartz, seized the opportunity offered by Gaudin's [49] first specimens of vitreous silica (1839) and

[39] Lippich, F., Sitzungsb. K. Akad. Wiss. Wien, Math.-Nat. Cl. (1890) **99**, IIa: 695-724.
[40] Landolt, H., Ber. Deutsch. Chem. Ges. (1894) **27**: 2872-2887.
[41] Peddie, W., Proc. Roy. Soc. Edinburgh (1882) **11**: 815-818.
[42] Wasastjerna, L., Oefv. Finska Vet. Soc. Förhandl. (1888-89) **31**: 167-177.
[43] Rose, Hermann, Neues Jahrb. Mineral, etc. (1910) Beil.-Bd. **29**, p. 79.
[44] Croullebois, Compt. rend. Acad. Sci. Paris (1875) **81**: 666-667.
[45] Soret, J. L., & Sarasin, E., Compt. rend. (1875) **81**: 610-613.
[46] Desains, P., Compt. rend. (1866) **62**: 1277-1279.
[47] Compt. rend. (1877) **84**: 1056-1060.
[48] Biot, Compt. rend. Acad. Sci. Paris (1839) **8**: 683-691.
[49] Gaudin, articles cited in VI, note [35].

tested its rotatory power, but could observe no effect. From this and other experiments he concluded that the rotatory power of quartz is not due to a molecular property but to a structure,—"un système de structure interne."

Mügge [50] could observe no optical rotation of sodium light in a column of well-polished vitreous silica plates 20 mm in total thickness.

S. P. Thompson,[51] and also Schulze,[52] report having been unable to detect any rotatory power in vitreous silica, and F. Bates, with the unexcelled facilities of the U. S. Bureau of Standards, also records the same negative result.

Herschel [53] sought to find out whether the molecule of silica is optically rotatory, by dissolving a dextro-rotatory crystal in caustic potash and examining the solution. The solution was found to possess no rotatory power whatever.

The form of the ray-surfaces in quartz

Theory involving axial birefringence

From the moment of the discovery of optical rotatory power in quartz, the problem of finding a mathematical or geometrical explanation for it in terms of the wave theory of light attracted the mathematical physicists.

Fresnel (1831) achieved the first success. The assumption that plane-polarized light travelling in the direction of the axis of a quartz crystal is separated into two circularly-polarized rays, of opposite sign and of different speeds, was shown by Fresnel to be entirely consistent with the phenomena. The two rays reunite on emerging from the quartz to form again a plane-polarized ray, rotated with respect to the original ray in accord with the difference in phase which has arisen between the two during their passage through the crystal.

This theory of the rotation in quartz has been confirmed quantitatively by Babinet (1837), Stefan [54] (1864), Lang (1869), and Cornu (1881), as well as by the complete agreement between this theory and the experiments of various other investigators. We need consider here only the experiments of Lang and of Cornu.

Lang [55] made a series of 63 observations on the refraction of the two rays in quartz with the incident light nearly parallel to the optic axis ($+4$ to $-5°$). He obtained the following values for the minimum of the indices:

Ordinary ray	7.3′
Extraordinary ray	44.2′
Mean	25.8′

[50] Mügge, article cited in VII, note [3].
[51] Quoted by Callendar, article cited in XX.
[52] Schulze, F. A., article cited in XXIII, note [10].
[53] Herschel, article cited in note [2].
[54] Stefan, J., Sitzungsb. K. Akad. Wiss. Wien, Math.-Nat. Cl. (1864) **50**, II: 380-393.
[55] Lang, V. von, Sitzungsb. K. Akad. Wiss. Wien, Math.-Nat. Cl. (1869) **60**, II: 767-794.

The measurements yielded the following indices at an angle of a few minutes to the axis:

Ordinary ray	1.544 188 7
Extraordinary ray	1.544 260 5
Difference	0.000 071 8

The difference does not change much with the angle, when near the axis.

The difference calculated from the best value of the rotatory power (Table XXXIII.1) is 0.000 071 3.

As Cornu[56] showed, the birefringence of quartz in the direction of the axis itself can be even more simply demonstrated by means of a prism cut with the optic axis parallel to one side of the base. If the base is an equilateral triangle and sodium light is incident at the angle for minimum deviation, passing parallel to the axis while within the crystal, two rays emerge separated by an angle of 27 seconds. If the prism is of dextro-quartz, the ray which is the less deviated of the two is found to be circularly polarized, with clockwise rotation; if it is levo-quartz, the ray which is the less deviated is found to be circularly polarized, with counter-clockwise rotation. If the original light is circularly polarized, only one ray emerges, polarized in the same sense as the original.

The existence of two waves is also shown by the production of two sets of interference bands, when half of a beam of white light is passed through a block of dextro-quartz and the other half through a block of levo-quartz of the same thickness. The two sets are fully separated if the thickness of quartz is over 30 mm.

By combining the two circularly polarized rays given by the prism first mentioned, with the ordinary ray given by a second prism attached to the first with faces in exactly the same plane, but with optic axis perpendicular to that in the first prism, Cornu was able to show that the speed of the ordinary ray is sensibly equal to the mean of the speeds of the two circularly polarized rays. This was tested for frequencies from cadmium No. 1 ($\lambda = 643.8$ mμ) to aluminum No. 32 in the ultra-violet ($\lambda = 185$). The precision of the comparison is low in the visible but much better in the ultra-violet because of the greater refraction. The record was made photographically.

A more satisfactory comparison was obtained by comparing interference bands. The first set is produced by two rays of white light which traverse, respectively, two blocks of quartz of exactly the same thickness, one along the optic axis and the other perpendicular thereto. If the incident light is plane polarized in a direction such that only the ordinary ray comes through the second block, two lateral systems of interference bands are obtained which are circularly polarized in opposite senses. The displacements of similar bands of each system are measured, and the mean is found to coincide exactly with the position of the central band of a second set, produced by shifting the two rays so that both traverse the first block of quartz.

The birefringence of quartz for radiation parallel to the optic axis cannot be shown by the autocollimation method of a ray reflected perpendicularly from the second face of a prism, with this face $\perp$ to the optic axis. The ray

[56] Cornu, A., Compt. rend. Acad. Sci. Paris (1882) **92**: 1365-1370.

entering the prism is separated into its two components, right and left circularly polarized, which are differently refracted and meet the second face at two distinct points. But each, when reflected, undergoes a change in its direction of rotation, with the result that the more refrangible entering ray becomes the less refrangible returning ray and vice versa, so that the two are practically recombined. The only effect is a slight broadening of the image of the spectral line used.

The recombination is not absolute, and becomes less perfect as the direction of the autocollimated ray deviates a little from the axis, as is necessary in order to produce a field of finite size. The allowable deviation corresponding to a given upper limit of resolution of the two images has not been calculated, but Straubel[57] has observed that with a deviation of 1.5′ a line remains satisfactorily sharp, as shown by displacing it in the field of a telescope having a subjective field of view of 36′ and 12-fold magnification.

The general theory

In the same year (1831) in which Fresnel demonstrated the character of the axial rotatory power of quartz, Airy proposed his theory of the transmission of radiation in directions at an angle to the principal axis. Airy assumed that the vibrations of the two sets of waves are elliptical, and also that the two wave-surfaces differ from those of a non-rotatory uniaxial substance only in being separated by a small but constant amount. The first part of this theory has been abundantly sustained by experiment, but the second has been found erroneous.

The true form of the wave-surfaces in quartz has developed out of theoretical contributions by Briot (1863), Willard Gibbs (1882), Gouy (1885), Wiener (1888), and experiments by Jamin (1850), Hecht (1883), Beaulard (1893), and others.[58]

Empirical relation of rotatory power to frequency

The rotatory power of quartz can be expressed mathematically with a high degree of exactness by a formula of the type suggested by Drude:

$$\rho = \frac{k_1}{\lambda^2 - \lambda_1^2} + \frac{k_2}{\lambda^2 - \lambda_2^2} + \ldots + \frac{k_n}{\lambda^2 - \lambda_n^2}$$

where $k_1, k_2 \ldots k_n, \lambda_1, \lambda_2, \ldots \lambda_n$ are constants. Although this was derived from a theoretical basis and λ_1, λ_2, etc., were given a theoretical significance, we may consider the formula, for present purposes, simply as an empirical formula connecting ρ and λ, and so write it thus:

$$\rho = \frac{k_1}{\lambda^2 - c_1} + \frac{k_2}{\lambda^2 - c_2} + \ldots + \frac{k_n}{\lambda^2 - c_n}$$

where $k_1, k_2, \ldots k_n, c_1, c_2, \ldots c_n$ are constants.

[57] Straubel, R., Ann. Physik (1902) **7**: 905-908.

[58] A good summary of the general theory is given by Pockels, F., *Lehrb. Kristalloptik* (1906) p. 307.

As shown by Lowry & Dickson [59] for certain organic compounds, a single term of this formula, namely,

$$\rho = \frac{k_1}{\lambda^2 - c_1}$$

will express the rotatory power within 0.04° over the greater part of the visible spectrum. The values of the constants for quartz are:

$$k_1 = 7.1764 \quad c_1 = 0.01677$$

when λ is expressed in μ (thousandths of a mm). These particular values of the constants were determined by Rupe & Akermann [60] from measurements at 4 frequencies, as a test of a proposed method of deriving formulas for the rotatory power of organic compounds.

To express the more accurate data of Lowry, extending far into the ultra-violet, a formula of 3 terms is necessary, namely:

$$\rho = k + \frac{k_1}{\lambda^2 - c_1} + \frac{k_2}{\lambda^2 - c_2}$$

in which

$$k = -0.1915 \quad k_1 = 9.5644 \quad k_2 = -2.3114 \quad c_1 = 0.012\ 742 \quad c_2 = 0.000\ 974$$

This represents the rotatory power in the visible region with an average error of only 0.0007° or about 0.003 per cent; and in the ultra-violet, with an average error of 0.003°, or about the same percentage. A preliminary comparison with new measurements in the ultra-red [61] indicates that the formula also holds in that region with an average deviation of 0.05°.

Historical note

Biot's early experiments indicated that $\rho = k/\lambda^2$. Later and more accurate measurements showed deviations from this formula, and it was therefore modified empirically by Boltzmann into the form

$$\rho = \frac{k_1}{\lambda^2} + \frac{k_2}{\lambda^4}$$

This formula still did not fit the data satisfactorily, and it was later replaced by Drude's formula, to which reference has already been made (see p. 669 and Chap. XXXVII).

[59] Lowry, T. M., & Dickson, T. W., Trans. Faraday Soc. (1914) **10**: 96-102.
[60] Rupe, H., & Akermann, A., Liebig's Ann. Chem. (1920) **420**: 1-32, especially p. 10.
[61] Lowry, T. M., article cited in note [59].

Chapter XXXIV. THE VARIATION OF REFRACTIVE PROPERTIES WITH TEMPERATURE

The speed with which radiation is transmitted within a substance (expressed by its index of refraction) is influenced by any change in the arrangement of the atomic centers, in their distances apart, in their state of motion, or in the arrangement of their electrons about the centers. Hence indices of refraction, rotatory power, and all their subsidiary constants, are affected by change of temperature.

Quantitative statement of the effect of temperature on index of refraction

When dealing with refractive data at a constant temperature we found it convenient, as well as consonant with experimental precision, to state indices of refraction of a substance as if either in air at the same temperature, or in air at 15°. When we come to state the change of index with temperature the admission of air becomes troublesome; shall the air be left at a constant temperature, or shall it be permitted to change with the substance? The latter condition is the more convenient for practical calculations, but for comparing properties the best plan is to remove the air entirely, and give the absolute index n and its change with temperature.

The temperature-effects may be expressed in ways entirely analogous to the constants of thermal expansion (see XX). It is customary to state the change directly, and not in the form of a coefficient. If the index is measured at two temperatures its average rate of change per degree, represented by Δn, is: $\Delta n = \frac{n_2 - n_1}{t_2 - t_1}$. When measured on a series of comparatively short intervals, the successive values of Δn form the material for a curve representing the quantity $\frac{dn}{dt}$. Integration of this curve furnishes the actual changes of index measured from the initial temperature.

Temperature-effects on the indices of silica

For quartz and vitreous silica at room temperature the rule holds that the *algebraic* value of the temperature-effect, dn/dt, decreases with increasing wave-length. The values of dn/dt for the two indices of quartz begin as positive magnitudes at short wave-lengths and pass through zero, becoming negative in the visible spectrum. For vitreous silica the quantity is positive, and relatively large, throughout the measured range of wave-length.

The change in the coefficient for a given change of wave-length is

approximately the same in both quartz and vitreous silica, as is shown by the following data:[1]

	$10^6 \frac{dn}{dt}$ for $\lambda = 206$	$10^6 \frac{dn}{dt}$ for $\lambda = 508$	Difference
Quartz (n_ϵ)	+ 0.63	— 7.29	7.92
Quartz (n_ω)	+ 1.19	— 6.35	7.54
Vitreous silica	+ 18.32	+ 10.21	8.11

The foregoing statements hold for the change of dn/dt with wave-length at a constant temperature, that of the atmosphere. With rising temperature, as with increasing wave-length, the indices of quartz decrease algebraically, and at a constantly accelerated rate as the inversion point is approached. At 573° there is a sudden drop in the indices. Above 573° the rate of change is positive, but the algebraic decrease of rate still continues.

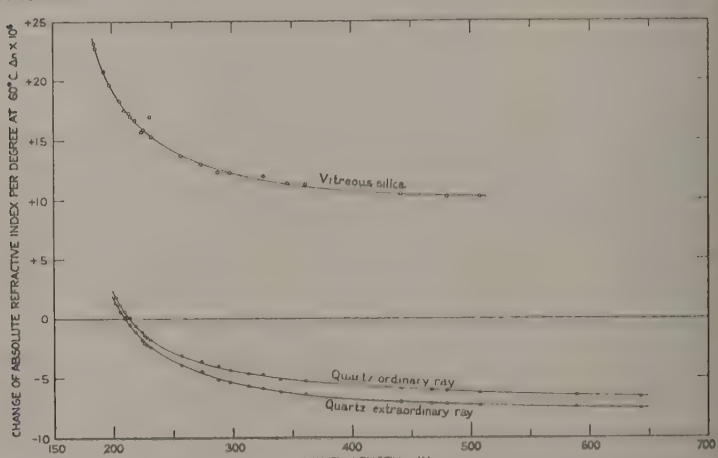


FIG. XXXIV.1.—Temperature coefficients of the absolute indices of quartz and vitreous silica, and their change with frequency.

The complete relationship of n, λ, and t may be represented by a model in three coordinates, consisting of three surfaces. The upper two surfaces represent n_ϵ and n_ω of quartz. They lie close together and nearly parallel. Each has a ridge whose summit line is inclined to the axes of t and of λ. The summit line has not been explored at temperatures below 0°, but very probably continues into that region. Toward higher tem-

[1] MARTENS, F. F., & MICHELI, F. J., Verhandl. Deut. Physikal. Ges. (1904) 6: 311-314.

peratures the two index-surfaces fall away with increasing steepness until at 573° both are broken off by a fault-scarp. Above 573° they rise, at first steeply, then with constantly diminishing slope.

The surface for vitreous silica lies entirely below the two just described, and rises continuously over the entire range of temperatures covered by the observations (—160 to 1000°C).

TABLE XXXIV.1.

MEAN TEMPERATURE-COEFFICIENTS OF THE REFRACTIVE INDICES OF QUARTZ. MICHELI, 1902.

Approximate wave-length mμ	Coefficient of absolute index		Coefficient of index in air	
	$10^6\Delta n_\epsilon$	$10^6\Delta n_\omega$	$10^6\Delta N_\epsilon$	$10^6\Delta N_\omega$
202	+ 1.29	+ 1.84	+ 2.67	+ 3.21
206	+ 0.63	+ 1.19	+ 1.98	+ 2.53
210	+ 0.08	+ 0.59	+ 1.43	+ 1.93
214	— 0.49	— 0.07	+ 0.83	+ 1.24
219	— 1.05	— 0.57	+ 0.27	+ 0.74
224	— 1.79	— 1.13	— 0.48	+ 0.17
226	— 2.04	— 1.36	— 0.75	— 0.08
228	— 2.22	— 1.55	— 0.93	— 0.27
231	— 2.41	— 1.80	— 1.12	— 0.52
257	— 3.89	— 3.09	— 2.65	— 1.86
274	— 4.44	— 3.55	— 3.23	— 2.35
288	— 5.06	— 3.99	— 3.85	— 2.79
298	— 5.34	— 4.29	— 4.15	— 3.11
313	— 5.68	— 4.65	— 4.50	— 3.48
325	— 5.87	— 4.69	— 4.69	— 3.52
340	— 6.17	— 5.08	— 5.01	— 3.93
361	— 6.40	— 5.32	— 5.25	— 4.18
441	— 7.05	— 5.87	— 5.93	— 4.75
467	— 7.15	— 5.96	— 6.01	— 4.85
480	— 7.22	— 6.10	— 6.10	— 4.99
508	— 7.29	— 6.25	— 6.16	— 5.14
589	— 7.54	— 6.50	— 6.42	— 5.39
643	— 7.64	— 6.60	— 6.53	— 5.49

THE EXPERIMENTAL DATA ON QUARTZ

The experimental data on the effect of temperature on the refractive indices of quartz fall naturally into two groups. The first group includes measurements made at temperatures not far from that of the atmosphere, yielding coefficients which are useful for correcting observed indices to a uniform temperature for comparison, but which do not indicate the course of change over any very considerable range. The second group includes measurements which approach or go beyond the high-low inversion-point at 573°.

Coefficients near room temperature have been recorded by Fizeau (1864), van der Willigen (1869-1870), Dufet (1884), Müller (1885), Pulfrich (1892), Gifford (1899-1902), Micheli (1902), Macé de Lépinay & Buisson (1904), Pérard (1922).

Reimerdes measured to 221° and Reed (1898) to 458°, while the change of refraction to and beyond 573° has been measured by Rinne & Kolb (1910). The birefringence, but not the separate indices, were measured up to 1050° by Mallard & Le Chatelier (1890), and Wright & Larsen (1909).

The most accurate and most extended set of measurements of the temperature coefficient of the refractive indices of quartz near room temperature are those made by Micheli[2] in 1902. Measurements were made at two temperatures (room temperature and 100°), and at 23 frequencies (6 visible, 17 ultraviolet). Records were made photographically, and the coefficients were obtained by a differential measurement on spectra at the two temperatures, taken on the same photographic plate.

The results, expressed in terms of the absolute index, are given in Table XXXIV.1, and are shown graphically in Figure XXXIV.1. The table contains also values of ΔN, the observed change of index in air whose temperature changes with that of the substance. These are useful for correcting measurements to a constant temperature or for figuring temperature changes in lenses.

Among the other investigators of the temperature-coefficient of refraction near room temperature, Fizeau, Dufet, and Gifford made measurements only with sodium light. Müller's were at several frequencies, but were of too low a precision to show with certainty the effect of the frequency; hence only his average value for all frequencies is used.

Their results, all reduced to absolute indices for sodium light, are given in Table XXXIV.2. The table also includes values by Pulfrich, by Reed, and by Pérard, which will be discussed more fully at a later page.

The results of Macé de Lépinay & Buisson for two of the cadmium rays have been referred to elsewhere (see p. 604).

TABLE XXXIV.2.

TEMPERATURE-COEFFICIENTS OF THE ABSOLUTE REFRACTIVE INDICES OF QUARTZ FOR SODIUM LIGHT, AS DETERMINED BY VARIOUS INVESTIGATORS.

Observer	Mean temp. ° C	$10^6\Delta n_\epsilon$	$10^6\Delta n_\omega$
Fizeau (1864)	20, 40	—7.14	—6.00
Müller (1885)	14.2	—6.30	—5.98
Dufet (1885)	20	—7.30	—6.26
Gifford (1902)	15	—7.86	—6.69
Gifford (1899)	22	.....	—6.38
Pérard (1922)	14	.....	—5.99
Pulfrich (1892)	59.6	—7.54	—6.38
Reed (1898)	61.2	—7.66	—6.07
Micheli (1902)	61.4	—7.54	—6.50

Fizeau's determinations[3] were made at the same time as his first measurements of the dilatation of quartz, and were made by his interferometer method,

[2] MICHELI, F. J., Arch. sci. phys. nat. (1902) (4) **13**: 217-243; Ann. Physik (1902) (4) **7**: 772-790.

[3] Article cited in XX, note [13].

depending on the displacement of the interference bands produced between light reflected at the upper and lower surfaces of a plate having faces plane but not quite parallel. To deduce the temperature-coefficient of the indices from such observations the thermal linear expansion coefficients must be known.

Fizeau's original values, calculated with the aid of his own expansion-coefficient data, were derived from measurements over two intervals, approximately 10 to 30° and 10 to 70°, and are as follows:

Mean temp.	$10^6\Delta N_\epsilon$	$10^6\Delta N_\omega$		
		Meas'd ∥ to axis	Meas'd ⊥ to axis	Mean
20	−6.28	−5.40	−5.35	−5.37
40	−6.61	−5.73	−5.44	−5.59

A recalculation by Dufet of Fizeau's optical data with the more reliable expansion coefficients of Benoit (p. 378) yields the values:

$$\Delta n_\epsilon = -7.14 \times 10^{-6},$$
$$\Delta n_\omega = -6.00 \times 10^{-6},$$

and indicates no change in the coefficient with rising temperature.

Müller[4] made a careful series of measurements to determine directly the change of the refractive indices of quartz with temperature. Measurements of both indices were made at 8 visible solar frequencies, each at 9 to 11 temperatures between 2 and 28°C, a total of 165 measurements.

The angle measurements were of high grade, but the prism was not as accurately cut as it might have been, and the author's method of relying upon natural changes of air temperature to secure his temperature-range is not conducive to the greatest accuracy. Nevertheless the precision seems to be about 5 to $10 \nearrow 10^{-6}$. The indices are better than the coefficients.

The precision was not sufficient to differentiate between the temperature coefficients for the highest and lowest frequencies. The dispersion of both indices seemed therefore nearly or quite independent of temperature, with the preponderance of evidence in favor of a slight decrease in dispersion with rising temperature. Later results by other investigators have confirmed the fact that the change of dispersion in the visible is small, but have shown that the small change which does exist is an increase, not a decrease, with temperature.

The data on the ordinary ray, which are the more precise, yielded values of $-10^6\Delta N_\omega$ varying from 4.02 to 5.31, average 4.47. The indices of the extraordinary ray were measured in a direction at 60° to the optic axis, and N_ϵ was therefore not obtained directly but by calculation involving N_ω. From the observed temperature coefficients I have estimated values of $-10^6\Delta N_\epsilon$ varying from 4.63 to 5.02, average 4.79, which is evidently low.

Pulfrich[5] made a considerable improvement in the reliability, accuracy, and ease of determination of both the temperature-coefficient of refraction and

[4] Müller, G., Publ. Astrophys. Obs. Potsdam (1885) **4**: 149-216.
[5] Pulfrich, C., Ann. Physik u. Chem. (1892) **45**: 609-665.

its variation with frequency, by the employment of Abbe's autocollimation method, modified by the use of a supplementary reflecting face on the prism. Measurements were made at 4 frequencies, of the change of index between 19.8 and 99.4°. The results are:

Solar line:	C	D	F	G'
$10^6\Delta n_\epsilon$	—7.61	—7.54	—7.15	—6.94
$10^6\Delta n_\omega$	—6.49	—6.38	—5.99	—5.77

Gifford[6] measured the coefficient for N_ω in sodium light, and subsequently redetermined it for both indices in connection with his precise measurements of the indices.[7] He observed that the coefficients increased approximately in proportion to the indices themselves, with decreasing wave-length.

Pérard's data, obtained over the range 5 to 23°C, have already been referred to (see p. 621). His rates for n_ω (absolute) are:

Radiation:	Hg	Hg	Hg	Cd
Wave-length ...	435.834	546.072	579.066	643.847
$10^6\Delta n_\omega$.....	5.56	5.85	5.96	6.15

Some temperature-coefficients deduced by van der Willigen[8] depend on a temperature-range of only a few degrees and are partly contradictory. They need not be considered further in comparison with the much more accurate data now available.

Change of the coefficient with temperature

The foregoing measurements have dealt with single intervals of temperature, without showing whether or not the rate changes with t. An inspection of Table XXXIV.2, however, indicates a tendency for the numerical value of the rate to increase with t. Such a change was established by Dufet's experiments.

Dufet[9] determined the rate of change of the indices of quartz for sodium light differentially, by observing the change with temperature of the Talbot fringes produced by light passing part through a prism of quartz in a heated thermostat, part through a prism of quartz at room temperature. Measurements were made both with the heated quartz at equilibrium, and with the heated quartz undergoing steady cooling, a specially determined correction being made in the second case for the difference in temperature between the cooling quartz and the cooling thermometer. As a result of 16 measurements on the ordinary and 18 measurements on the extraordinary ray, the following

[6] Gifford, J. W., British Assoc. Rep. 1899: 661-662.
[7] p. 337 of article cited in XXXI, note [4].
[8] Articles cited in XXXI, note [36].
[9] Dufet, H., Bull. Soc. Min. France (1885) **8**: 171-304; J. de Physique (1885) (2) **4**: 389-419.

formulas for the temperature coefficients were obtained, good between 0 and 100°:

$$10^6 \frac{dn_\epsilon}{dt} = -7.246 - 0.0034\,t$$

$$10^6 \frac{dn_\omega}{dt} = -6.227 - 0.0008\,t$$

An independent check was furnished by differential measurements of the temperature-coefficient of the birefringence, which yielded (see p. 684)

$$10^6 \frac{d(n_\epsilon - n_\omega)}{dt} = -972 - 3.2\,t$$

By combining this formula with the two for $\frac{dn_\epsilon}{dt}$ and $\frac{dn_\omega}{dt}$, and weighting them in accordance with the average deviation of their data, the following final values were obtained:

$$10^6 \frac{dn_\epsilon}{dt} = -7.223 - 0.0037\,t$$

$$10^6 \frac{dn_\omega}{dt} = -6.248 - 0.0005\,t$$

Strictly speaking, these are coefficients of the indices referred to air at a constant temperature, but they are practically the same as the coefficients of the absolute indices.

Data at higher temperatures

Reimerdes [10] was the first to extend the measurements on the temperature-coefficient of the refraction of quartz beyond 100°. He made a series of determinations on N_ω with green mercury light, $\lambda = 546.072$ mμ, using Fizeau's method, which depends upon a knowledge of the linear thermal expansion of the substance in the direction in which the light passes through it. Measurements were made on 6 temperature intervals, yielding mean temperatures from 30 to 221°. The results are plotted in Figure XXXIV.2. They are based on Reimerdes' own expansion data, which are somewhat low (see p. 385), but the original measurements are not reported in sufficient detail to permit of their recalculation.

Reimerdes' results are represented best by his formula:

$$10^6 \frac{dn_\omega}{dt} = -5.882 + 0.00272\,t - 0.000\,053\,3\,t^2$$

The integration of this curve yields the actual change of index over the range covered, and if the value of n_ω for $\lambda = 546$ mμ in Table XXX.2 be taken as a basis, a curve of the actual index can be constructed. This curve is included in Figure XXXIV.4.

[10] Article cited in XX, note [24].

Reed[11] extended the measurements on the temperature-coefficient to still higher temperatures. He measured the change of index differentially, using Abbe's method as modified by Pulfrich. Determinations were made at 4 frequencies, and on 8 temperature intervals covering the range from room temperature to 458°. The light sources were a sodium flame, and a hydrogen-mercury tube which supplied the two hydrogen lines corresponding to C and F and the mercury line 435.

Table XXXIV.3 contains the values of Δn as published. In Table XXXIV.4 I have reconstructed the intervals and calculated the actual indices at the temperatures of observation, basing them upon indices taken from Table XXX.2.

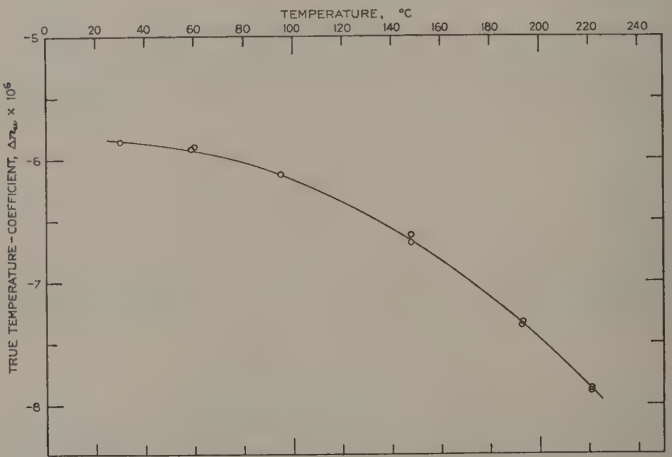


FIG. XXXIV.2.—Reimerdes' measurements of the rate of change with temperature of the absolute index n_ω of quartz.

The most extended series of measurements on the change of refraction of quartz with temperature is that of Rinne & Kolb.[12] They measured both of the indices for 10 frequencies at 10 temperatures, from —45 to 765°C. In addition, measurements were made for 4 frequencies at —140°. The method of minimum deviation was used, on the natural 60-degree prism of crystals from Skole, Galicia. The source of light was a Nernst lamp, from which frequencies corresponding to the principal lines of the solar spectrum were selected by a Wülfing monochromator, calibrated by means of a helium tube and also by comparison with the solar lines themselves.

[11] REED, J. O., *Ueber den Einfluss der Temperatur auf die Brechung und Dispersion einiger Gläser und Krystalle*, Inaug.-Diss. Jena, 1897, 53 pp., 1 pl.; Ann. Physik u. Chem. (1898) **65**: 707-744.

[12] RINNE, F., & KOLB, R., Neues Jahrb. Min. 1910, **II**: 138-158.

TABLE XXXIV.3.

TEMPERATURE COEFFICIENTS OF THE ABSOLUTE INDICES OF REFRACTION OF QUARTZ. REED, 1897.

Mean temp. °C	$-10^6\Delta n_\epsilon$				$-10^6\Delta n_\omega$			
	Hg	"F"	"D"	"C"	Hg	"F"	"D"	"C"
61.2	7.07	7.23	7.66	7.73	5.61	5.72	6.07	6.15
125.2	7.71	7.89	8.29	8.43	6.10	6.27	6.73	6.91
177.0	8.73	8.90	9.33	9.44	6.80	6.92	7.60	7.71
227.5	9.52	9.77	10.12	10.30	7.71	7.88	8.42	8.54
275	11.06	11.33	11.78	11.91	8.64	8.88	9.49	9.67
328	13.48	13.75	14.19	14.27	11.07	11.26	11.84	11.99
385	17.53	17.88	18.40	18.59	14.91	15.17	15.68	15.85
435	21.49	21.91	22.53	22.75	18.26	18.60	19.27	19.52

The precision is about 0.0001 at room temperature, and somewhat less than this at the high and low temperatures. Although this is not a high precision compared with the best data at room temperature, it is more than balanced by the wide range of temperature covered, supplying data available from no other source.

The complete results, which I have recalculated to absolute indices, are given in Table XXXIV.5.

The data of Rinne & Kolb, Reed, and Reimerdes are compared graphically in Figures XXXIV.3 and XXXIV.4. The agreement is fairly good, considering the difficulties of measuring indices at high temperatures, but it could be better. The differences are systematic in character, and give the appearance of being due to the measurements of temperature rather than to the measurements of index.

Historical note

Rudberg [12] was the first to measure the change in the indices of quartz with temperature. A change of 64°C (20 to 84) apparently reduced the deviation of both rays by the same amount, namely, 42.0″. This is equivalent to the values: $\Delta N_\epsilon = -4.4 \times 10^{-6}$, $\Delta N_\omega = -4.0 \times 10^{-6}$.

EXPERIMENTAL DATA ON THE CHANGE OF BIREFRINGENCE OF QUARTZ WITH TEMPERATURE

The birefringence at various temperatures may be found by subtracting n_ω from n_ϵ in the preceding Tables in this chapter, but it can be directly measured with greater precision (see p. 634). Such measurements have been made by Dufet (1885) near room temperature, and by Mallard & LeChatelier (1890) and Wright & Larsen (1909) at higher temperatures. Mallard & Le Chatelier examined the effect of frequency in detail, but at

[12] RUDBERG, F., Ann. Physik u. Chem. (Poggendorff) (1832) **26**: 291-301.

TABLE XXXIV.4.

ABSOLUTE INDICES OF QUARTZ AT VARIOUS TEMPERATURES, BASED UPON INDICES FROM TABLE XXX.2 AND CALCULATED WITH THE DATA OF REED (1897).

Radiation	Wave-length mμ	23.0° C	99.4	151	203	252	298	358	412	458
					EXTRAORDINARY INDEX, n_ϵ					
Hg	435.834	1.563 62	1.563 08	1.562 69	1.562 23	1.561 76	1.561 26	1.560 45	1.559 50	1.558 51
H ("F")	486.133	1.559 37	1.558 82	1.558 41	1.557 95	1.557 47	1.556 95	1.556 12	1.555 16	1.554 15
Na (Mean) .	589.29	1.553 74	1.553 16	1.552 73	1.552 24	1.551 75	1.551 21	1.550 35	1.549 36	1.548 32
H ("C")	656.278	1.551 31	1.550 72	1.550 29	1.549 80	1.549 29	1.548 74	1.547 89	1.546 88	1.545 84
					ORDINARY INDEX, n_ω					
Hg	435.834	1.554 19	1.553 76	1.553 45	1.553 10	1.552 72	1.552 32	1.551 66	1.550 85	1.550 01
H	486.133	1.550 08	1.549 64	1.549 32	1.548 96	1.548 57	1.548 17	1.547 49	1.546 67	1.545 82
Na	589.29	1.544 64	1.544 17	1.543 83	1.543 43	1.543 02	1.542 58	1.541 87	1.541 03	1.540 14
H	656.278	1.542 29	1.541 82	1.541 46	1.541 06	1.540 64	1.540 20	1.539 48	1.538 62	1.537 72

TABLE XXXIV.5.

REFRACTIVE INDICES OF QUARTZ AT VARIOUS TEMPERATURES, AS MEASURED BY RINNE & KOLB (1910) AND RECALCULATED AS ABSOLUTE INDICES.

Solar line	Wave-length mμ	— 140° C	— 45°	23°	115°	212°	305°	410°	550°	580°	650°	765°
					EXTRAORDINARY INDEX, n_ϵ							
G′ (Hγ)	434.047	....	1.5633	1.5634	1.5629	1.5623	1.5615	1.5598	1.5551	1.5503	1.5521	1.5532
(d)	466.8	....	1.5609	1.5608	1.5603	1.5597	1.5588	1.5572	1.5526	1.5478	1.5492	1.5506
F	486.133	1.5594	1.5594	1.5593	1.5589	1.5581	1.5573	1.5558	1.5512	1.5464	1.5475	1.5490
(c)	495.75	....	1.5587	1.5587	1.5582	1.5576	1.5567	1.5552	1.5503	1.5456	1.5468	1.5481
b_2	517.27	....	1.5574	1.5574	1.5568	1.5562	1.5553	1.5538	1.5488	1.5442	1.5454	1.5469
D_2	588.997	1.5541	1.5539	1.5537	1.5532	1.5526	1.5515	1.5499	1.5451	1.5405	1.5417	1.5431
α	627.8	1.5526	1.5525	1.5522	1.5517	1.5510	1.5500	1.5486	1.5437	1.5389	1.5403	1.5416
C	656.278	....	1.5516	1.5513	1.5508	1.5502	1.5491	1.5475	1.5427	1.5380	1.5393	1.5406
B	687.2	1.5506	1.5506	1.5504	1.5499	1.5492	1.5481	1.5466	1.5419	1.5369	1.5383	1.5397
a	718.9	....	1.5499	1.5495	1.5490	1.5483	1.5472	1.5458	1.5408	1.5362	1.5375	1.5388
					ORDINARY INDEX, n_ω							
G′ (Hγ)	434.047	....	1.5539	1.5540	1.5536	1.5531	1.5523	1.5510	1.5469	1.5425	1.5439	1.5454
(d)	466.8	....	1.5515	1.5514	1.5511	1.5506	1.5498	1.5483	1.5442	1.5400	1.5414	1.5429
F	486.133	1.5504	1.5501	1.5500	1.5497	1.5491	1.5483	1.5469	1.5426	1.5385	1.5399	1.5414
(c)	495.75	....	1.5494	1.5494	1.5491	1.5485	1.5477	1.5465	1.5421	1.5379	1.5393	1.5406
b_2	517.27	....	1.5481	1.5481	1.5476	1.5472	1.5463	1.5452	1.5407	1.5363	1.5377	1.5392
D_2	588.997	1.5449	1.5448	1.5446	1.5441	1.5437	1.5428	1.5414	1.5370	1.5329	1.5341	1.5356
α	627.8	1.5434	1.5434	1.5431	1.5427	1.5422	1.5413	1.5401	1.5357	1.5314	1.5328	1.5340
C	656.278	....	1.5425	1.5423	1.5418	1.5414	1.5405	1.5390	1.5349	1.5304	1.5319	1.5331
B	687.2	1.5417	1.5416	1.5414	1.5410	1.5405	1.5395	1.5382	1.5337	1.5296	1.5309	1.5321
a	718.9	....	1.5408	1.5405	1.5401	1.5396	1.5386	1.5374	1.5327	1.5288	1.5301	1.5313

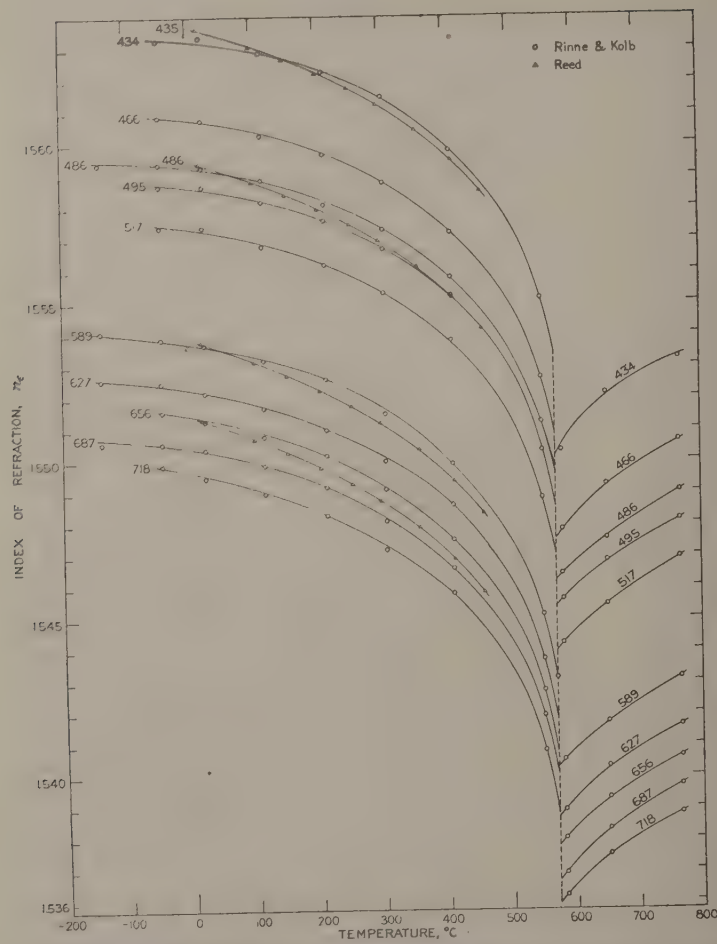


FIG. XXXIV.3. Comparison of experimental data on refractive indices of quartz at various temperatures and for various frequencies. Extraordinary ray, absolute index n^e. (The first three digits of the wave-length are placed near the curve for that wave-length.)

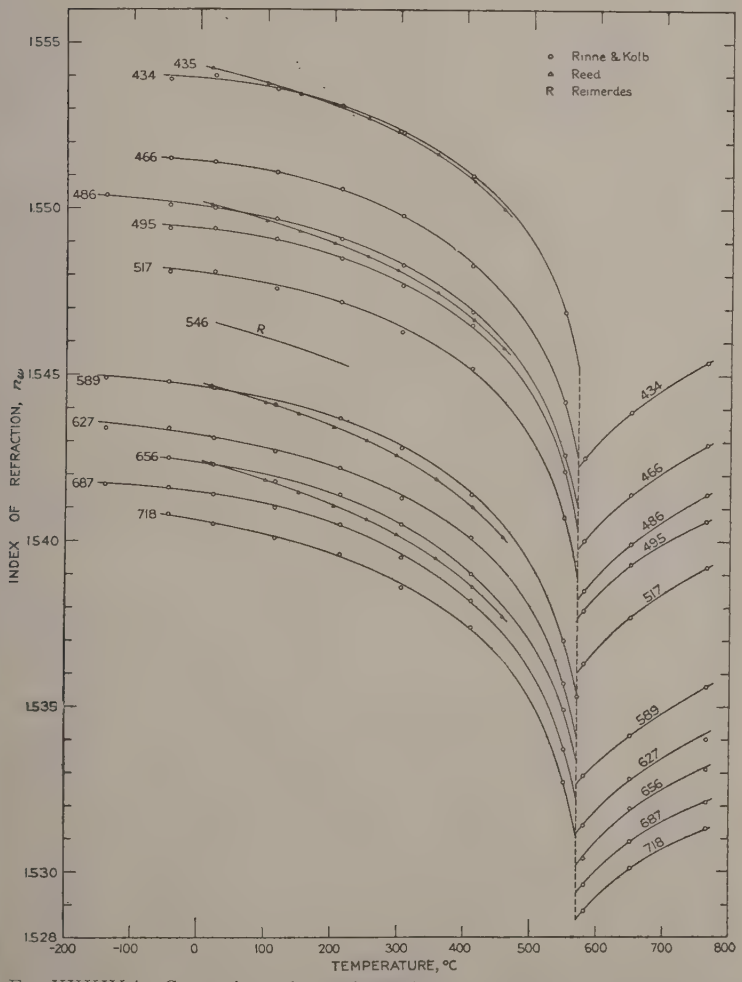


FIG. XXXIV.4.—Comparison of experimental data on refractive indices of quartz at various temperatures and for various frequencies. Ordinary ray, absolute index n_ω. (The first three digits of the wave-length are placed near the curve for that wave-length.)

rather widely separated temperatures, while Wright & Larsen, employing only two frequencies, took numerous readings at short intervals of temperature.

Dufet[14] determined the variation of the birefringence of quartz with temperature by a differential interference method. As the result of measurements at 15 temperatures between 4 and 99° he obtained the following formula:

$$B = B_0 - (972\,t + 1.6\,t^3)\ 10^{-9}$$

The coefficient of t is estimated by the author to be accurate to 0.8 per cent, and of t^3, to 4 per cent.

Wright & Larsen[15] measured the birefringence of quartz in a "thermal microscope" consisting of the usual petrographic microscope with a small water-cooled platinum resistance furnace mounted on its stage. Readings were made with the Babinet compensator, both in white light and in sodium and lithium monochromatic light, at about 120 temperatures between 12° and 1359°C. Temperatures were read with a platinum-platinrhodium thermel and millivoltmeter. Four different plates of quartz, cut parallel to the axis, were employed. The results were corrected for thermal expansion, with the aid of Le Chatelier's coefficients (p. 381). The measurements in monochromatic light are better than in white, and those in sodium light are the more satisfactory of the two monochromatic sets. The latter data are represented in Figure XXXIV.5. Since the monochromatic measurements extend only to about 850°, they are supplemented in the Figure by a set of measurements in white light above 950°, which serve to show the direction of the change with temperature.

Mallard & Le Chatelier[16] used three methods: (1) measurement of the movement of the neutral band of a compensator in line with two quartz plates, one of which is heated; (2) the observation of Fizeau-Foucault interference bands, produced by the two plates of quartz as above, with polarizing and analyzing prisms and a spectroscope; (3) photographic recording of the Fizeau-Foucault bands. The last method furnished the most accurate results.

Measurements were made at 11 to 15 frequencies (wave-lengths 393 to 587 mμ at the widest) at temperatures of 15, 220, 530, 590, 660, and 1050°C. The data are expressed in terms of empirical formulas, first for the effect of frequency alone at each fixed temperature, and then, by combining these formulas, for the effect of temperature and frequency simultaneously.

The effect of the frequency on the retardation due to a plate which starts at 0°C with a thickness of 1 mm is expressed by the formula: $R = a + \frac{b}{\lambda^2}$, in which R is the retardation, λ is the wave-length in μ, and a and b are constants at a given temperature. The changes in a and b with temperature are then expressed as quadratic or linear functions of t. These data need not be given here in detail.

[14] Article cited in note [9].

[15] Wright, F. E., & Larsen, E. S., Amer. J. Sci. (1909) **27**: 421-447; Zeitschr. anorg. Chem. (1910) **68**: 338-369.

[16] Mallard, E., & Le Chatelier, H., *Sur la variation qu'éprouvent, avec la température, les biréfringences du quartz . . .*, Bull. Soc. Franc. Min. (1890) **13**: 123-129; Ann. Chim. et Phys. (1895) (7) **6**: 90-114.

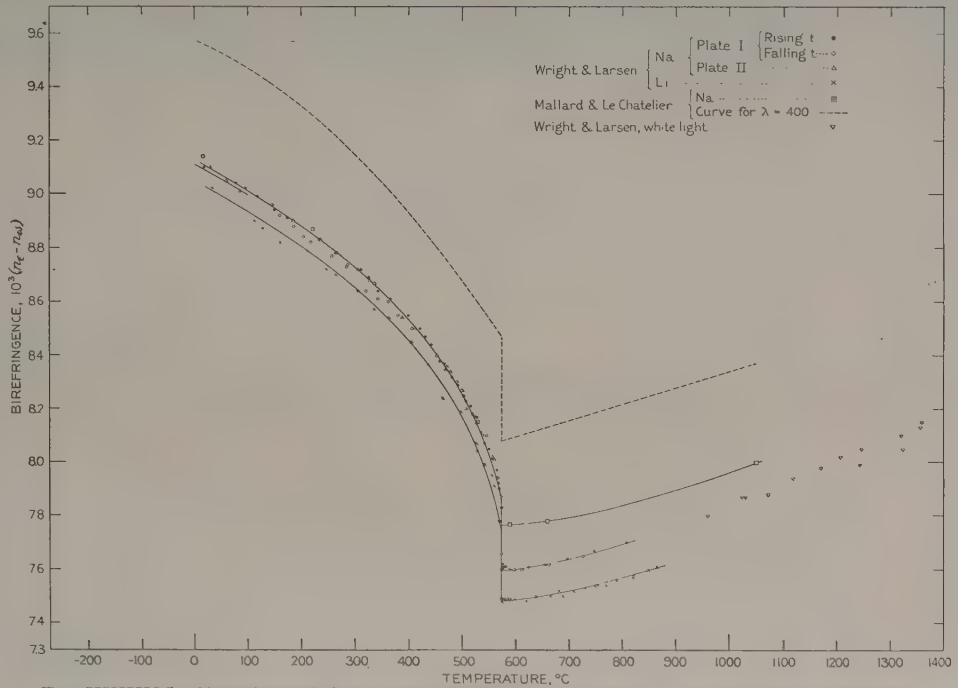


FIG. XXXIV.5.—Experimental data on the change of birefringence of quartz with temperature.

Finally, the resulting formulas are further reduced to actual values of birefringence by dividing R by the quantity $1 + \delta_m\, t$, which represents the increase in thickness of a 1-mm plate due to thermal dilatation. The use of Le Chatelier's coefficients for the linear expansion yields the following, below 573°:

$$10^6 B = 8782.4\,(1 - 104.7 \times 10^{-6} t - 0.2094 \times 10^{-6} t^2) + 126.8\,(1 + 56.9 \times 10^{-6} t)\frac{1}{\lambda^2}$$

and above 573°:

$$10^6 B = \left(7432 + 103.6\frac{1}{\lambda^2}\right)[1 + 0.000\ 075\ 5\ (t - 570)]$$

The measurements at 590° lie somewhat above the high-temperature curve.

TABLE XXXIV.6.

CHANGE OF REFRACTIVE INDEX OF VITREOUS SILICA PER DEGREE, AT 60° C. MARTENS, 1904.

Radiation	Approx. wave-length	Change of absolute index. $10^6 \Delta n$	Change of index in air. $10^6 \Delta N$
Al	185	23.19	24.61
Al	186	22.71	24.13
Al	193	20.80	22.17
Al	198	19.65	21.00
Zn	206	18.32	19.64
Zn	210	17.50	18.81
Cd	214	17.28	18.57
Zn	215	17.01	18.30
Cd	219	16.66	17.94
Cd	224	15.70	16.97
Cd	226	15.90	17.16
Cd	231	16.99	18.24
Cd	232	15.26	16.51
Cd	257	13.74	14.95
Cd	274	13.01	14.20
Cd	288	12.32	13.49
Cd	298	12.25	13.41
Cd	325.5	11.99	13.14
Cd	346	11.41	12.55
Cd	361	11.27	12.40
Cd	441	10.41	11.51
Cd	480	10.20	11.29
Cd	508	10.21	11.29

Better expansion coefficients than Le Chatelier's are now available, but the correction is so small that there would be no great gain in recalculating the formulas.

Mallard & Le Chatelier's data for sodium light are included in Figure XXXIV.5. The agreement with Wright & Larsen is very close up to the inversion point, but the two curves separate above that temperature.

Included in the same Figure is Mallard & Le Chatelier's curve for $\lambda = 400$ mμ, which will serve to show the amount of dispersion of the birefringence. The character of the curvature, however, is noticeably different from Wright & Larsen's; the latter is undoubtedly the more correct, being based on many more temperatures. There is also included a short curve, basing on the indices

in Table XXX.2, and showing Dufet's rate of change of birefringence, which is seen to be in good agreement with Wright & Larsen.

Perrier [17] has confirmed previous observations as to the general character of the change of birefringence of quartz with temperature. He found the sudden decrease to occur at 582°, and followed the increase which takes place above the inversion as far as 1000°C. On cooling, the sudden change was found to occur about 3° lower than on heating.

The experimental data on vitreous silica

The principal measurements on the influence of temperature on the refractive index of vitreous silica are by Martens, who worked near room temperature, and Rinne, who carried the measurements to 1000°.

Martens [18] used Micheli's very precise method (see p. 674) on a prism cut from vitreous silica made by Heraeus. With 4 photographic plates, measurements were made for 23 frequencies between wave-lengths 185 and 656 mμ. The results are given in Table XXXIV.6, and are included in Figure XXXIV.1. The mean temperature to which the values of ΔN and Δn apply is 59.8°C.

Rinne [19] determined the relation of the refractive index of vitreous silica (source not stated) to temperature, for 4 visible frequencies of helium. Measurements were made at 9 temperatures, from —160° to 1000°C, using a prism and the minimum-deviation method on a goniometer reading to 2 seconds. The results, which I have recalculated to absolute indices, are presented in Table XXXIV.7 and Figure XXXIV.6. In the three curves which are carried to 1000° there is an easily observed irregularity in the vicinity of 600°, which is reminiscent of the less marked irregularity in the dilatation of vitreous silica in this same region (see p. 402), and which is suggestively near to the inversion-temperature of quartz. It is too large, and also too uniformly present in the three curves, to be due to errors of measurement in the index, although it is conceivably explainable by a concealed error in the temperature. Additional measurements in this vicinity would be interesting.

Table XXXIV.7.

Absolute Index of Refraction of Vitreous Silica at Various Temperatures, Calculated from Data of Rinne, 1914.

Temp. ° C	He blue λ = 471.315 mμ	He green 501.568	He yellow 587.563	He red 667.815
— 160	1.4635	1.4617	1.4581	1.4559
— 64	1.4641	1.4624	1.4586	1.4563
18	1.4649	1.4629	1.4592	1.4569
130	1.4660	1.4642	1.4604	1.4579
235	1.4675	1.4654	1.4616	1.4591
365	1.4692	1.4672	1.4633	1.4608
475	1.4708	1.4689	1.4649	1.4625
590	1.4722	1.4703	1.4663	1.4639
1000	....	1.4772	1.4729	1.4706

[17] Perrier, A., Arch. sci. phys. nat. (1916) (4) **41**: 492-497.
[18] Martens, F. F., Verh. Deut. Physik. Ges. (1904) **6**: 308-311.
[19] Article cited in XXX, note [18].

Cristobalite

The refractive index of cristobalite for sodium light decreases at the inversion-point. The index of high-cristobalite must be nearly the same as that of vitreous silica at the same temperature, since in the mixture of glass and cristobalite formed by heating a piece of vitreous silica at 1450° or higher no crystals can be seen until the inversion starts at about 230°.[20]

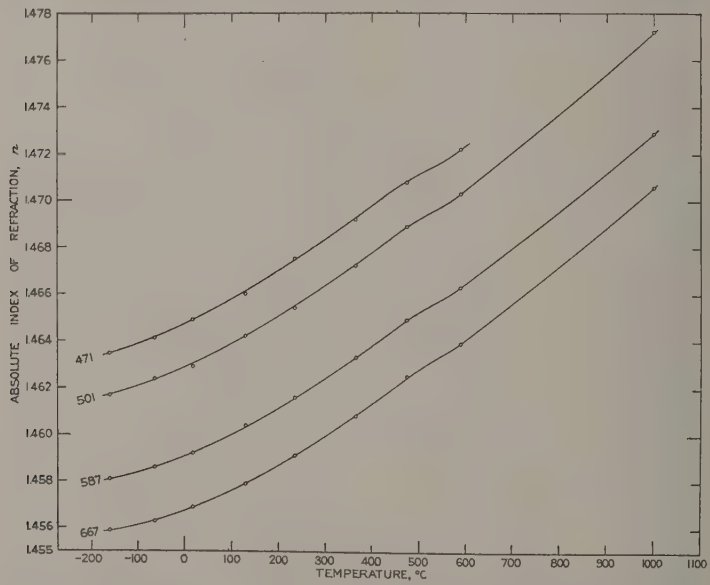


Fig. XXXIV.6.—Experimental data on the change of index of refraction of vitreous silica with temperature and frequency. (The first three digits of the wave-length are placed near the curve for that wave-length.)

Influence of temperature upon rotatory power

Quantitative statement of the effect

The simplest mode of stating rotatory power is in circular degrees per mm thickness, measured in the direction of the optic axis. The complete specification must also include the wave-length of the radiation and the temperature.

The quantity actually measured, when data are wanted at various temperatures, is the total rotation of a particular plate of the substance.

[20] Rieke & Endell, article cited in VI, note [87].

The reduction of such data to rotation per mm therefore requires a knowledge of the coefficient of linear expansion over the entire range.

But no particularly useful purpose seems to be served by reducing all the data to 1 mm. Furthermore, the high-temperature expansion may not be known with exactness. The expansion at room temperature, on the other hand, is usually known quite well enough to permit the measurements of thickness of the plate, which are always made at room temperature, to be reduced to any selected common temperature as a standard.

It seems best, therefore, to express the rotation of a crystalline substance in circular degrees for a plate which was 1 mm thick at some standard temperature, say 0°C or 20°C, and which is permitted to assume its natural dimensions at other temperatures.

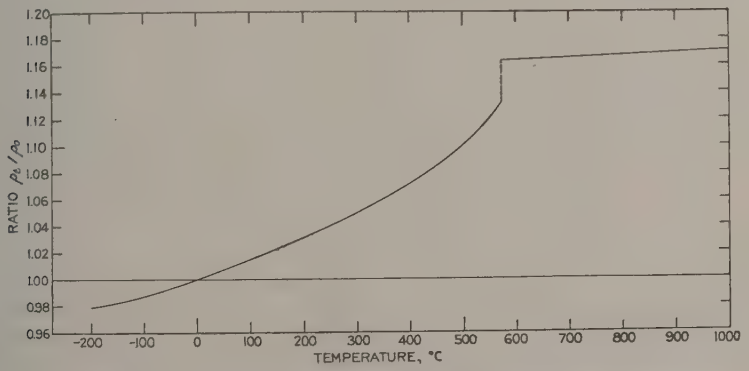


FIG. XXXIV.7.—Change of the rotatory power of quartz with temperature, uncorrected for thermal expansion.

INFLUENCE OF TEMPERATURE UPON THE ROTATORY POWER OF QUARTZ

The rotatory power of quartz increases with the temperature. The rate of increase at room temperature is about 0.014 per cent per degree.

The rate becomes greater as the temperature rises, culminating in a sudden increase of 4.3 per cent at the inversion-point, 573°. Above 573° the rotatory power continues to increase but at a rate only about one-tenth of that at room temperature.

At all temperatures the percentage rate is independent of the frequency of the radiation, within the limits of measurement, for the visible and the ultra-red. The rate is apparently a little higher in the ultra-violet.

The manner of change of rotatory power with temperature is shown in Figure XXXIV.7.

TABLE XXXIV.8.

EXPERIMENTAL DATA ON THE MEAN COEFFICIENT, ε, OF THE THERMAL CHANGE OF ROTATORY POWER, CALCULATED FROM THE ORIGINAL EXPERIMENTAL DATA.

$$\rho_t = \rho_0 (1 + \epsilon t)$$

Author	t	$10^6\varepsilon$	Range of temp. °C	Range of wave-length mμ
Fizeau (1864)	72	121	12 to 72	589 only
Lang (1875)	94	146	20 to 94	535 to 670
Sohncke (1878)	100	38	23 to 100	430 to 656
	172	153	15 to 172	486 to 656
	54	121	15 to 54	589 only
	72	119	15 to 72	589 only
	94	131	15 to 94	589 only
	135	145	15 to 135	589 only
	173	154	15 to 173	589 only
Gumlich (1896)	30	139	8 to 30	589 only
Gumlich (1898)	19	134	1 to 19	436 to 656
	47	140	1 to 48	436 to 656
	73	145	1 to 74	436 to 656
	100	150	1 to 100	436 to 656
Macé de Lépinay (1900)	19	180	13 to 19	546 only
Bates (1906)	6.2	146	4.8 to 6.2	546 only
	8.3	150	4.8 to 8.3	546 only
	16.0	135	5 to 16	546 only
	20.8	139	5 to 21	546 only
	29.6	144	5 to 30	546 only
	44.6	145	5 to 45	546 only
	49.8	146	5 to 50	546 only
Ingersoll (1917)	130	165	20 to 141	589 to 1800
Soret & Guye (1893)	— 42	126	23 to — 42	589 only
	— 55	124	23 to — 55	589 only
	— 71	119	18 to — 71	589 only
Becquerel (1908)	— 188	111	Room to — 188	589 only
Molby (1910)	— 117	126	23 to — 117	508 to 520
	— 138	121	24 to — 138	436 only
	— 155	118	23 to — 155	508 to 520
	— 177	112	24 to — 178	436 to 546
	— 188	110	23 to — 189	436 to 643
Joûbert (1879)	— 20	136	— 20 to 0	589 only
	100	150	0 to 100	589 only
	357	179	0 to 357	589 only
	445	187	0 to 445	589 only
	778	214	0 to 778	589 only
Le Chatelier (1889)	280	163	20 to 280	448 to 656
	415	181	20 to 415	448 to 656
	560	221	20 to 560	448 to 656
	600	273	20 to 600	448 to 656
	900	187	20 to 900	448 to 656

The experimental data

The data on the effect of temperature on the rotatory power of quartz fall naturally into two groups: (1), measurements near room temperature, and (2), measurements covering a wider range of temperature.

In the first group we have the experiments of Fizeau (1864), Lang

(1876), Sohncke (1878), Gumlich (1896-1898), Macé de Lépinay (1900), Bates (1906), for visible frequencies, and Ingersoll (1917) for the ultra-red. The second group includes Soret & Guye (1893), Becquerel (1908), and Molby (1910), all below 0°; and Joubert (1878), and Le Chatelier (1889), at higher temperatures.

The actual temperature-effect in the rotatory power changes greatly with the frequency, as the rotatory power itself does, but the percentage change based on the value at some standard temperature is almost independent of frequency. Hence the change is best stated in the same way as compressibility and thermal dilatation (see XX), by means of a "coefficient,"—either the true coefficient $\frac{1}{\rho_0} \cdot \frac{d\rho}{dt}$ or the mean coefficient $\frac{1}{\rho_0} \cdot \frac{\rho_t - \rho_0}{t - t_0}$.

The greater part of the experimental results are best compared by recalculating them all to values of the mean coefficient from 0°, represented by ε in the formula: $\rho = \rho_0 (1 + \varepsilon t)$. This I have done in Table XXXIV.8. In most cases correction has been made for the interval between 0° and the initial temperature of measurement either by means of the author's own formula, or if he used only a single interval, with Gumlich's formula (Table XXXIV.9).

The coefficients given by the investigators themselves for the change of the coefficient with temperature are listed in Table XXXIV.9. The mean coefficient from 0° is related to the coefficients in the Table thus: $\varepsilon = a + bt$.

TABLE XXXIV.9.

VALUES GIVEN BY VARIOUS AUTHORS FOR THE COEFFICIENTS IN THE FORMULA $\rho = \rho_0 (1 + at + bt^2)$

Observer	Range of temperature °C	Range of wave-length mμ	$10^4 a$	$10^6 b$
Sohncke (1878)	15 to 173	486 to 656	99.9	0.318
Joubert (1879)	−20 to 100	589	146.3	0.0329
	0 to 350	589	135.8	0.132
Le Chatelier (1889)	0 to 570	279 to 656	96	0.217
Gumlich (1898)	0 to 100	436 to 656	131	0.195
Soret & Guye (1893)....	−71 to 20	589	144.2	0.350

Measurements on single intervals

Fizeau [21] observed an increase of 1.4 degrees in the rotation of a plate 8.96 mm thick when heated from 11.5 to 72.0°C; initial rotation, 194.97. Right- and left-quartz gave identical results.

Lang [22] measured differentially the change of rotatory power of quartz with temperature for sodium, thallium, and lithium light. He made 42 determinations at room temperature and 100°, using Broch's method, and basing the measurements on the three sources mentioned, without attempting to determine

[21] Article cited in XX, note [18].

[22] LANG, V. VON, Sitzungsb. Akad. Wiss. Wien (1875) 71, II: 707-714.

accurately their absolute rotations. The results, expressed as temperature-coefficients $\times 10^6$ of the rotatory power for the range 20 to 94°C, are: 149 ± 5 for Li, 144 ± 5 for Na, 153 ± 4 for Tl; mean 149. No definite relation to frequency is detectable.

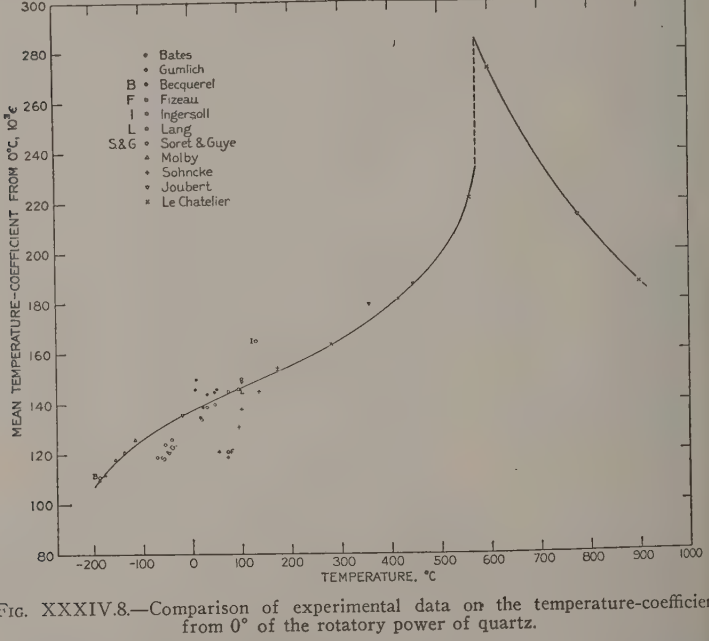


FIG. XXXIV.8.—Comparison of experimental data on the temperature-coefficient from 0° of the rotatory power of quartz.

Gumlich [23] made measurements in sodium light at various temperatures between 8 and 30°C, dependence being placed upon natural and artificial changes in the temperature of the air in the laboratory. The precision of this method is not sufficient to indicate definitely any change of the coefficient with temperature. The coefficient obtained, using 20° as the basic temperature, is 147×10^{-6}.

A value of 180×10^{-6} by Macé de Lépinay [24] is based on only a short interval, although the measurements were of good precision. Schönrock [25] called attention to the considerable difference between this value and Gumlich's, but believed that a real difference of this magnitude might be possible.

Incidentally to his measurements of natural and magnetic rotatory power, Ingersoll [26] determined the approximate temperature-coefficients of the natural

[23] Article cited in XXXIII, note [6].
[24] p. 645 of article cited in XXXIII, note [16].
[25] Zeitschr. Instrum. (1901) **21**: 90-92.
[26] p. 263 of article cited in XXXIII, note [27].

rotatory power of quartz at 5 frequencies, partly in the ultra-red. The specimen was heated in air, and its temperature measured by means of a near-by mercury thermometer, so the results are not of the highest precision. Within their limit of accuracy they indicate no change in the coefficient with frequency. The results are:

λ in μ:	0.589	0.800	1.00	1.50	1.80	Mean
Lower temp.	39	21	20	20	20	24
Upper temp.	129	141	141	125	113	130
$10^6 \frac{1}{\rho} \cdot \frac{\Delta\rho}{\Delta t}$	164	185	152	156	166	165

Measurements over a series of intervals

Sohncke [27] was the first to observe that the temperature-coefficient is not constant, but increases with t. He measured the rotatory power of a plate of left-quartz about 12 mm thick at 6 temperatures between 15 and 173°C, and at the 5 solar frequencies C, D. E, F, and G, using Broch's method (p. 665). Like Lang, Sohncke could detect no effect of frequency larger than the experimental error.

Gumlich [28] determined the change of the rotatory power for 4 visible frequencies ($\lambda = 436$ to 656 mμ) by measurements at 5 temperatures between 0° and 100°, on a thickness of 39 mm of quartz. His results, like those already quoted, show no definite change with frequency. I have calculated the following mean coefficients from the published data:

Wave-length	t	$10^6\varepsilon$	t	$10^6\varepsilon$	t	$10^6\varepsilon$	t	$10^6\varepsilon$
436	18.8	135	46.8	142	74.2	148	99.6	153
546	18.7	133	48.3	138	73.1	142	99.5	148
579	18.5	133	46.7	139	72.5	144	99.5	150
656	18.3	135	46.7	142	73.8	145	99.6	150
Mean	18.6	134	47.1	140	73.4	145	99.5	150

Bates [29] made a careful determination of the coefficient for mercury green light ($\lambda = 546$ mμ), controlling the temperature between 5 and 50° by means of a water cell. He gives only the average coefficient for 7 intervals, which is 10^6 (144 ± 0.87). But if the first two intervals, which are very short, be omitted, a definite increase with temperature is noticeable.

Determinations of the coefficient at low temperatures were begun by Soret & Guye [30]. They made measurements at 4 temperatures between room temperature and —71°, with sodium light only, on a 60-mm specimen previously used by Soret & Sarasin. Their results are included in Tables XXXIII.3 and XXXIV.9.

[27] Sohncke, L., Ann. Phys. u. Chem. (Wiedemann) (1878) **3**: 516-531.
[28] pp. 352-358 of article cited in XXXIII, note [21].
[29] p. 245 of article cited in XXXIII, note [14].
[30] Soret, C., & Guye, C. E., Arch. sci. phys. nat. (1893) (3) **29**: 242-255.

The most extensive low-temperature data are those of Molby [21], who measured the rotatory power of quartz at the temperatures of the room and of liquid air for 10 visible frequencies, and also at a number of intermediate temperatures for sodium light and a few other frequencies. He used a polarimeter of the Lippich type, with a spectroscope and color screens to provide monochromatic radiations from flame or arc sources. In the first set of measurements both dextro-quartz and levo-quartz specimens of thickness 2.86 mm were examined. The average rotation of the two at —190° for a plate 1 mm thick at 20°, for sodium light, is 21.196 degrees; at 20.8°, 21.693. The two were not separately calculated because of variations in zero setting.

Higher precision was attained in the second set of measurements [22], the results of which, corrected to round temperatures with the help of the coefficients 144×10^{-6} per degree at room temperature and 70×10^{-6} at —188°, are shown in Table XXXIV.10. These were made on two specimens of dextro-quartz of total thickness 6.6095 mm, and two of levo-quartz of total thickness 6.6490 mm.

The fairly constant difference between the dextro- and levo-quartz is probably due to a constant error, since two of the four plates were not perfectly plane-parallel.

TABLE XXXIV.10.

ROTATORY POWER OF QUARTZ AT 20° AND —188° C, PER MM AT 20°. MOLBY, 1910.

Radiation	Wave-length mμ	ρ at 20°		ρ at —188°		Average percentage change, 20 to —188°
		Levo	Dextro	Levo	Dextro	
Hg lamp	404.7	48.830	48.842	47.631	47.675	2.422
Hg lamp	435.9	41.403	41.441	40.427	40.469	2.353
Ag-Cd arc	467.0	35.477	35.529	34.638	34.696	2.354
Ag-Cd arc	480.0	33.580	33.593	32.782	32.818	2.344
Ag-Cd arc	508.6	29.625	29.656	28.930	28.983	2.310
Ag-Cd arc	520.9	28.153	.....	27.501	.....	2.319
Hg lamp	546.1	25.467	25.472	24.868	24.885	2.328
Na flame	589.3	21.667	21.686	21.169	21.188	2.314
Ag-Cd arc	643.8	17.997	18.003	17.561	17.603	2.329
Li flame	670.8	16.488	16.493	16.150	16.145	2.086

If the first and last values in the table be left out of account because of the diminished accuracy due to lower visual sensitivity at the limits of the spectrum, it is evident that the proportional change in rotatory power between 20 and —188° is very nearly the same for all frequencies. There is a slight drift toward a lower rate of change at longer wave-lengths, but the mean value 2.33 per cent will represent the observed rotations within 0.02 per cent.

Since the change of rotatory power with temperature is so nearly independent of frequency, various measurements by Molby at intermediate temperatures and at several frequencies may be combined by the assumption

[21] MOLBY, F. A., Physical Rev. (1909) **28**: 57-63.
[22] MOLBY, F. A., Physical Rev. (1910) **31**: 291-310.

of proportionality of differences into a single curve. The values of the mean coefficient of rotatory power so obtained (which I have calculated from the published results) are included in Table XXXIV.8 and Figure XXXIV.8.

Molby has enough data near —180° to furnish a fairly reliable value for the true temperature-coefficient at liquid air temperatures:

Wave-length	Temp. range	$10^6 . \frac{1}{\rho} . \frac{d\rho}{dt}$
435.9	— 188.0 to — 175.4	79
508.6	— 189 to — 178	69
520.9	— 189 to — 178	60
546.1	— 189 to — 177.2	65
Mean	— 183	68

The results obtained by Becquerel [33] are in good agreement with the foregoing. He found ρ for sodium light to be 21.71 degrees per mm at room temperature and 21.20 at —188°, a decrease of 2.35 per cent. He also noted that the percentage decrease is practically independent of frequency.

Joubert [34] covered a wider range of temperature than any other investigator of rotatory power. Using the Laurent polarimeter method on 10 specimens of quartz of thicknesses 15 to 40 mm, he made measurements at various temperatures (7 published) between —20 and about 1500°C, in sodium light. An additional set of measurements made by the method of Fizeau & Foucault at room temperature and at the boiling point of sulfur (445°), with solar lines C, D, and F, showed that the ratios of the rotatory powers for these three frequencies were the same at both temperatures; in other words, the temperature coefficient of the rotatory power is independent of the frequency between C and F.

The quartz specimens were contained in an evacuated glass or porcelain tube, heated by boiling alcohol, water, aniline, mercury, sulfur, or cadmium. The highest temperatures were obtained by means of a Deville crude-oil burner. The temperature 1500° was evidently only estimated roughly from the color or brightness.

The published results are given below. I have corrected the temperatures to correspond to the present accepted boiling points:

$t =$	— 20	0	100	357	445	778	1500(?)
$\rho =$	21.599	21.658	21.982	23.040	23.464	25.259	25.420

As luck would have it, Joubert's series of boiling points left a wide gap about the region of the inversion-point of quartz, so that although he recognized that the manner of change of rotatory power with temperature was very different at temperatures above 800° and below 300°, he failed to observe the high-low inversion, which remained undiscovered for another ten years.

Le Chatelier's measurements [35] were made on a plate 16.65 mm thick, with sodium light and with 4 frequencies of the magnesium spark spectrum, and at

[33] Becquerel, J., Compt. rend. Acad. Paris (1908) **147**: 1281-1284.
[34] Joubert, J., J. de Physique (1879) **8**: 5-10.
[35] Le Chatelier, H., *Sur la polarisation rotatoire du quartz*, Compt. rend. Acad. Paris (1889) **109**: 264-266; Bull. Soc. Franc. Min. (1890) **13**: 119-123.

8 temperatures between room temperature and 900°C. The results are given in Table XXXIV.11. The precision is about 0.1 degree except for the ultra-violet radiation 279, which was observed photographically and which could not be determined closer than about 2 degrees.

The results of both Joubert and Le Chatelier are shown graphically in Figure XXXIV.8.

TABLE XXXIV.11.

RELATION OF THE ROTATORY POWER OF QUARTZ TO TEMPERATURE AND FREQUENCY. LE CHATELIER, 1889.

Temp. °C	$\lambda = 279$	448	500	518	589	656
20	114.5	39.24	30.78	28.62	21.72	17.25
280	....	40.80	32.16	29.82	22.68	18.06
415	....	42.00	32.90	30.60	23.40	18.60
475	127.	....	....	....	....	....
560	....	44.10	34.56	32.04	24.30	19.38
600	....	45.60	35.76	33.18	25.26	20.10
650	131.	....	....	....	....	....
900	132.	45.84	36.	33.24	25.32	....

As far as can be told from the results of Le Chatelier, the temperature-coefficient of the rotatory power is independent of frequency. Below 573°, the results are expressed by the formula:

$$\rho_t = \rho_o \ (1 + 96 \times 10^{-6}\, t + 0.217 \times 10^{-6}\, t^2)$$

while above 573° the change is small, and is expressible by:

$$\rho_t = \rho_o \ [1.165 + 15 \times 10^{-6} \ (t - 570)]$$

The sudden increase at the inversion point is 0.043ρ.

Wright & Larsen [36] measured the rotatory power of 9 specimens of quartz in their thermal microscope, using small plates perpendicular to the axis and a bi-quartz wedge plate, with sodium light. Measurements were made at 60 temperatures between 17 and 850°C. The method is not very sensitive and the results are not as precise as those of Le Chatelier, but the average values agree with Le Chatelier's curve within the limits of error.

Perrier has also confirmed the observations already described on the effect of temperature on the rotatory power of quartz. He found the inversion-point (sudden increase) at 582°, the increase continuing at a much slower rate at higher temperatures. On cooling, the phenomena are exactly reversed except for the familiar temperature-hysteresis at the inversion.

Bates, also, has confirmed the slower rate of increase above 573°.

None of the results thus far quoted shows any certain and unmistakable influence of frequency upon the temperature-coefficient, either in the visible or ultra-red region. The only evidence of any change with frequency is contained in the data on the ultra-violet.

Soret & Sarasin [37] did not attempt to determine the temperature-coefficient

[36] p. 431 of article cited in note [25].
[37] Article cited in XXXIII, note [23].

of rotatory power in their series of measurements, since they made nearly all readings at temperatures near 20°, and any of the existing formulas was exact enough to correct the results to 20°. Some of their measurements on the farthest ultra-violet rays of cadmium, however, happened to be at temperatures as low as 13.3°, and here they found definite evidence that the coefficient was higher than that which they had been using. This difference was confirmed by further measurements made over the range 5.3 to 20.6°C on rays 24 and 25, which showed that the coefficient for these frequencies is 179×10^{-6}, instead of about 147×10^{-6}, the value for the visible spectrum. The upward drift of the coefficient with decreasing wave-length, as seen in Molby's data, is evidently real.

Historical notes

While experimenting on the effect of temperature on the rotatory power of sugar solutions, Dubrunfaut, in 1846, suspected that the rotatory power of quartz might be variable with temperature, and made some special experiments to decide the question. He found an increase of about 1.4 per cent accompanying a change of temperature from 20 to 70°C; while if he heated a plate of quartz with an alcohol lamp to a temperature below a red heat he produced an increase of about 11 per cent.

Gernez described in 1879 a differential method of determining the change of rotatory power of quartz with temperature, consisting in mounting two quartz plates in series, one right-rotating and one left, of the same thickness. One of the plates is then heated while the other is kept at room temperature, and the resulting departure from the original zero rotation is measured by Broch's method. Although Gernez's device was evidently tested experimentally, no numerical data were ever published.

Chapter XXXV. REFLECTION

When radiant energy passes from a vacuum into a substance, or across the boundary from one substance to another, there is always a certain amount of *reflection* or throwing back of energy into the medium from which it came. Although reflection would thus appear to be an interphase or surface property, it is so closely related to the radiational constants of the substances concerned that it is properly considered here, in association with refraction, emission, and absorption.

General principles of reflection

In Chapter XXX the forms of silica served as examples to show how the propagation of radiant energy within a substance depends upon the symmetry of the substance and upon the relation of the radiant wave to the axes and planes of symmetry, and also upon certain characteristic constants, the refractive indices. Another complication is now added, that of a boundary plane between the given substance and some other. Reflection and refraction at the boundary are the result.

It is obvious that several new combinations of conditions are now possible, involving the relation of the boundary surface both to the wave and to the symmetry.

In the general case there are two sets of waves propagated within the substance. From any point on the boundary, then, four sets of waves will diverge, two refracted and two reflected. Conditions of symmetry, with respect to the substance, the wave, or the surface, may reduce the total number to three, two, or one. Their direction, their energy, and their state of polarization can be derived from general principles, involving the use of no other specific constants than those already considered in previous chapters. The principles need not, therefore, be considered here, especially since there are very few data on the reflection by silica of radiation to which it is transparent.

Quantitative measure of reflection

The amount of energy reflected at a surface may have any value from a few per cent up to practically one hundred per cent. The most perfect reflection is that which sometimes occurs when the attempt is made to send radiant energy from a denser into a rarer medium,—from quartz into air or water for example,—at an angle of incidence which is greater than a certain critical value depending on the indices of refraction of the two substances. Under these circumstances, so-called *total reflection* occurs.

Under conditions other than those which give this kind of total reflection, the percentage of energy reflected can usually be predicted very closely

on the assumption that the change from one medium to the other is abrupt; that is, that there is no layer having properties different from those of the contiguous substances. The general principles of reflection already alluded to contain this assumption.

The actual percentage reflected, however, is often found to differ from that expected, and in ways to which no general principles can yet be applied. It is necessary to make specific experiments with the surfaces concerned. Abnormal effects of this kind have not been shown to exist in the forms of silica; neither, on the other hand, has their absence been definitely proved, except in the case of dry well-polished quartz, which reflects visible frequencies in the normal manner.

Reflection of the ultra-red by silica

While the reflecting power of silica for visible light has offered nothing of special interest, it has been quite otherwise with the ultra-red spectrum. Quartz has been one of the principal substances on which the guiding experiments on ultra-red reflection have been made.

In one part of the ultra-red spectrum quartz reflects almost like a polished metallic surface, namely, at about 8.5 to 9 μ. Fairly strong reflections are also present at 12 to 13 μ, and again at 21 to 26 μ.

Vitreous silica shows maxima of reflecting power at about the same frequencies as quartz, but the maxima are of much less intensity.

Tridymite and cristobalite have not been examined.

Micro-crystalline silica reflects very similarly to quartz, through the portion of the spectrum where the principal bands (9, 12, 21 μ) occur. Beyond 30 μ micro-crystalline silica differs from quartz and vitreous silica in having a weak minimum of reflection at about 80 μ. In this it resembles opal and some of the silicate glasses, which have a weak minimum in the same region.

Reflection of polarized light by quartz

When analyzed in detail, the intensity and state of polarization of the radiation reflected by quartz is seen to be a complicated resultant of the state of polarization of the incident rays, their inclination to the axis of the quartz, and the inclination of the reflecting surface both to the axis and to the incident rays.[1] The simplest case is that of reflection of light falling perpendicularly on a surface which is $\perp$ to the axis, just as the simplest case of transmission is that of light traveling $\parallel$ to the axis. A single ray, corresponding to the "ordinary" refracted ray (p. 587) is reflected, and the intensity is the same whether the original radiation is polarized or not. Most of the experimental work in the ultra-red has been with such a surface, $\perp$ to the axis.

[1] For a detailed discussion of the case of radiation passing from an isotropic substance into a uniaxial crystalline substance (the case of air to quartz) see Wood, *Lehrb. d. Kristalloptik* (1906), pp. 183-195.

For other surfaces the effects differ according to the polarization of the incident ray. Radiation vibrating || to the axis and incident normally upon a surface || to the axis gives the other extreme case, that of reflection corresponding to the extraordinary ray. If $R_\perp$ and $R_\parallel$ are the intensities reflected from surfaces $\perp$ and || to the axis, respectively, when unpolarized radiation is incident; R_ω is the intensity reflected from a surface $\perp$ to the axis when plane-polarized radiation vibrating $\perp$ to the axis is incident; and R_ϵ is the intensity reflected from a surface || to the axis when plane-polarized radiation vibrating || to the axis is incident; then

$$R_\omega = R_\perp \qquad R_\epsilon = 2R_\parallel - R_\perp$$

Liebisch & Rubens [2] used this relation to test the completeness of polarization of their ultra-red of wave-length 22 μ, with the following results for the percentage reflection from quartz:

Radiation	R_ϵ	R_ω
Unpolarized	24.3	59.3
Polarized	24.4	59.5

The curves of reflection of R_ϵ and R_ω for quartz are compared in Figure XXXV.3. Where the reflection is small, the two intensities are hardly distinguishable. In the vicinity of the absorption bands the two intensities differ, and for the longer wave-lengths the maxima are not at the same wave-length. If the ultra-red could be seen, a crystal of quartz would show varying surface colors when viewed through a rotating Nicol prism.

Experimental data on reflection of the visible spectrum

Koenigsberger [3] made a series of measurements of the reflecting power of quartz for visible radiation, in support of a proposal to make quartz a standard for reflecting power, since metals and alloys are not sufficiently reproducible. Plates of quartz cut $\perp$ to the axis were used. The results are assembled in Table XXXV.1.

As is evident from the Table, an old plate of quartz gave values which are about 3.3 per cent lower than the theoretical, for both of the frequencies employed. This difference persisted after the plate had been cleaned, wiped, and passed through a Bunsen flame. A suggested explanation is that the difference is due to a surface layer of different properties, an effect often observed in silicate glasses, in which the reflection may be as much as 30 per cent less than the theoretical (Rayleigh). If it be assumed that the slightly abnormal angle of polarization found by Jamin for light reflected from quartz is due to a surface film, then the index of refraction and the percentage reflection from this film can be calculated, yielding the value 4.36 per cent at 650 mμ, in close agreement with that found.

[2] p. 207 of article cited in note [14].

[3] Koenigsberger, J., *Ueber Quarz als Reflexionsnormale*, Physik. Zeitschr. (1903) **4**: 494-495.

The agreement is misleading, however, because the assumption of a surface film is not necessary in order to explain the data. Microscopic examination of the surface of the old plate showed that its polish was imperfect, the surface retaining scratches and pits from the original grinding of the plate. The low reflecting power is probably due to scattering or diffuse reflection by this roughened surface.

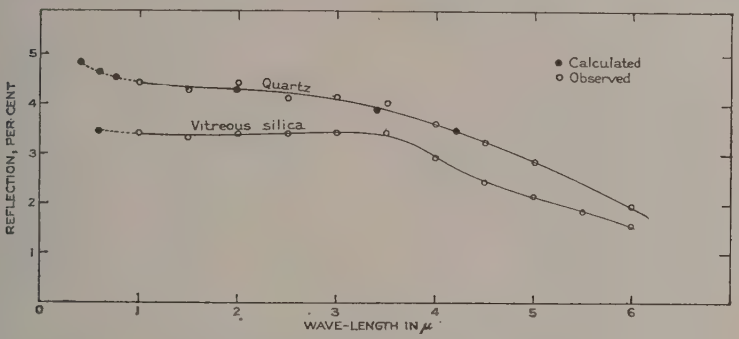


FIG. XXXV.1.—Measured reflecting power of quartz and vitreous silica for wave-lengths of 1 to 6 μ. (Reinkober, 1910.)

This explanation is confirmed by the data on the new and well-polished plate, which gave values of reflecting power in agreement with theory, within the limits of error. The reflecting power of this plate suffered no measurable change when the plate was wiped and moistened with water, provided it was well dried afterwards. The plate also showed no change in reflection after standing for six weeks.

TABLE XXXV.1.

REFLECTING POWER OF QUARTZ FOR VISIBLE RADIATION. KOENIGSBERGER, 1903.

Values given are percentages.

	Wave-length mμ	Old plate, 1 mm thick, ordinary polish	New plate, highly polished	Reflection calculated from index of refraction
r_2 = observed total of reflection from both faces	600	8.46 [a]	8.73 [d]	8.73
	...	8.40 [b]	8.79 [e]	...
	...	8.42 [c]	8.75 [f]	...
r_1 = reflection from single face [g]	600	4.41	4.58	4.56
Reflection from single face	650	4.38	...	4.54

[a] Mean of 20 readings; average deviation 0.02.
[b] New set-up of apparatus.
[c] Best value.
[d] Comparative measurement, by comparison with old plate.
[e] Absolute measurement.
[f] General mean.
[g] $r_2 = \frac{2r_1}{1 + r_1}$.

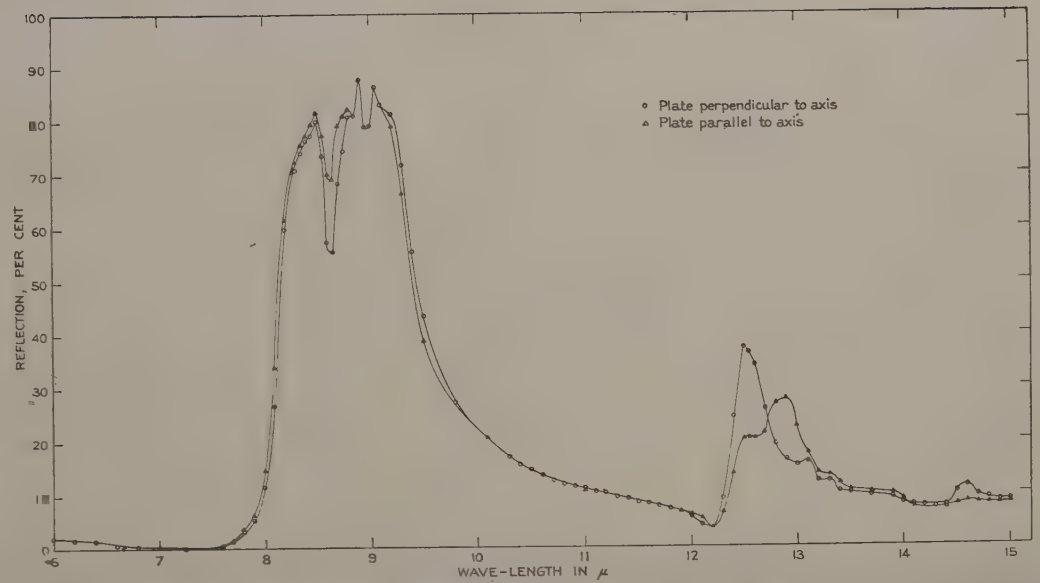


FIG. XXXV.2.—Measured reflecting power of plates of quartz parallel and perpendicular to the axis, for unpolarized radiation of wave-lengths 6 to 15 μ. (Reinkober, 1910.)

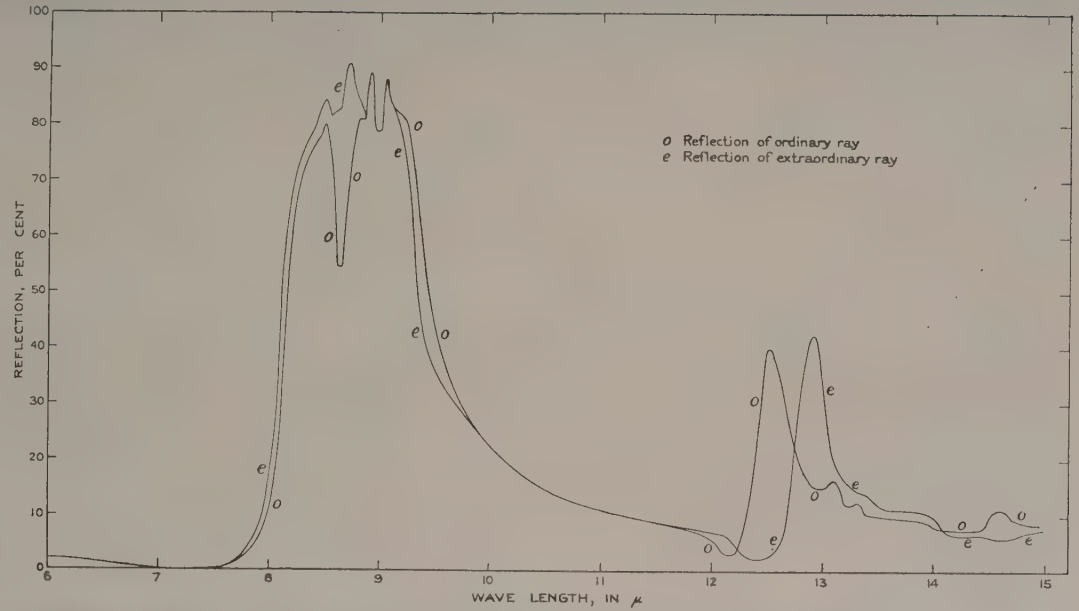


FIG. XXXV.3.—True reflecting power of quartz for plane-polarized radiation of wave-lengths 6 to 15 μ, corresponding to the ordinary and extraordinary refracted rays. (Reinkober, 1910.)

The experimental data in the ultra-red

The experimental researches group themselves naturally about the principal reflection bands of silica at 8 to 9 μ and 20 to 27 μ. They are concerned mainly with quartz, and to a less extent with vitreous silica, while a few measurements have been made also on micro-crystalline (chalcedonic) silica. Tridymite and cristobalite have not been examined.

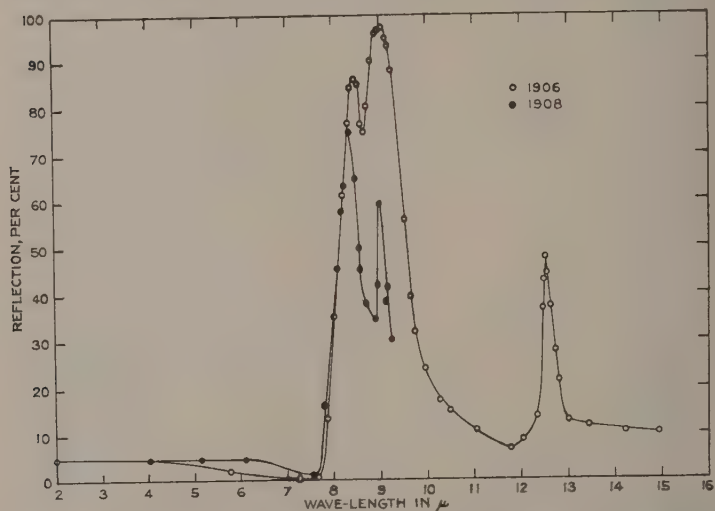


Fig. XXXV.4. Measured reflecting power of quartz, with surface perpendicular to axis. (Coblentz, 1906-1908.) A curve published in 1911 (see note [18]) agrees closely with the 1906 curve, except that it shows evidence of the doubled maximum at 8.4 μ (see Fig. XXXV.3.)

Measurements on quartz in the near ultra-red

Our most detailed knowledge of the reflecting power of quartz in the near ultra-red (1 to 20 μ) comes from the work of Reinkober, who examined the bands closely and differentiated between the ordinary and extraordinary rays. Other data of good precision are supplied by Coblentz, by Schaefer & Schubert, and by Rubens & Hertz. The first measurements made on the bands at 8 to 9 μ, those by Nichols, may be somewhat in error because of inhomogeneous radiation, which may account for the difference between Nichols' curve and that obtained shortly after by Rosenthal. Other data on the position and intensity of these bands were obtained by Rubens & Nichols and by Trowbridge & Wood.

Reinkober[4] measured the reflecting powers of quartz and vitreous silica for ultra-red radiation of wave-lengths 1 to 18 μ, and also the transparency of vitreous silica for the same range. Measurements were made at intervals of 0.1 or 0.05 μ, and were comparative, the energy reflected or transmitted by the substance being received on a sensitive thermopile whose galvanometer deflections were compared with those produced by reflection from a silvered mirror.

The results obtained by Reinkober on quartz are represented in Figures XXXV.1, 2, and 3. Figure XXXV.1 shows the observed reflecting power of both quartz and vitreous silica at frequencies of 1 to 6 μ, and Figure XXXV.2 gives the observed results on quartz from 6 to 15 μ. The measurements on quartz were made on plates both ⊥ and ∥ to the axis, using unpolarized radiation.

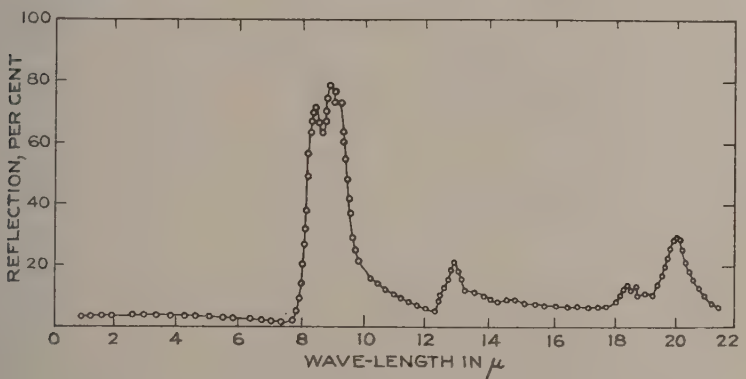


FIG. XXXV.5.—Measured reflecting power of compact vein quartz. (Schaefer & Schubert, 1921.)

Figure XXXV.3 contains the derived curve (see p. 700) of reflection for the extraordinary ray (*e*) and the measured curve for the ordinary ray (*o*), both corrected for slit width according to Runge.

When the reflection is small, vibrations equivalent to the extraordinary and ordinary rays are nearly equally reflected by quartz. Furthermore, the percentage agrees very closely with that calculated from the indices of refraction, as shown by the calculated points in Figure XXXV.1.

Coblentz[5] measured the reflecting power of quartz on a surface ⊥ to the axis. A Nernst oxide filament formed the source of the radiations. The reflection was compared with that of silver deposited upon glass. Reflection was at an angle of 25 degrees, and the results are therefore slightly higher than the true value, the maximum correction being 2 per cent. Since the

[4] REINKOBER, O., *Ueber Absorption und Reflexion ultraroter Strahlen durch Quarz, Turmalin und Diamant*, Inaug.-Diss. Berlin, 1910, 39 pp. Ann. Physik (1911) (4) **34**: 343-372.

[5] COBLENTZ, W. W., *Investigations of infra-red spectra*, Parts III and IV, Carnegie Inst. Washington, Publ. **65** (1906), 128 pp., especially p. 80.

variations due to the surfaces of the specimens themselves are of this order of magnitude, no correction was made on account of the angle. Wave-lengths were measured by means of a mirror spectrometer and rock-salt prism, and intensities with a Nichols radiometer. Measurements were made over the range 2 to 15 μ.

A supplementary investigation[6] published in 1908 was made with a fluorite prism in place of the rock-salt prism in the spectrometer, and a bolometer in place of the radiometer. The precision was thus improved, because the dispersion of fluorite is several times that of rock salt. The region 4 to 9.5 μ was studied for both quartz and vitreous silica.

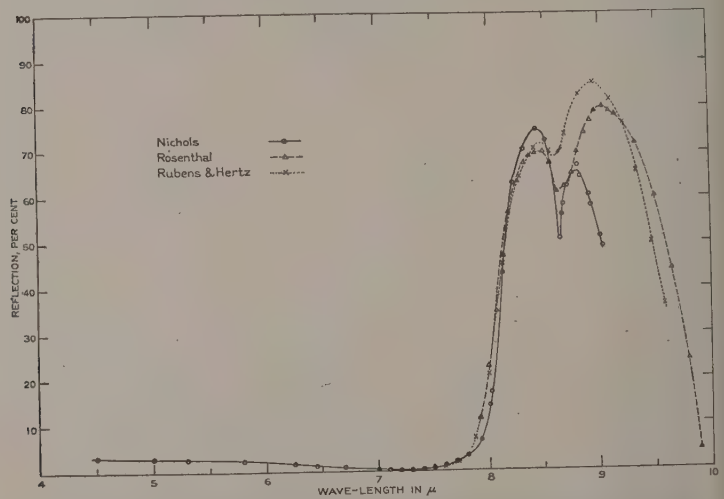


FIG. XXXV.6.—Reflecting power of quartz (surface perpendicular to axis) as measured by Nichols (1897), by Rosenthal (1899), and by Rubens & Hertz (1912).

The results of the two series on quartz are shown in Figure XXXV.4. Further data on quartz published in 1911 (see note [18]) agree closely with the 1906 curve.

Schaefer & Schubert[7] measured the reflecting power of quartz, microcrystalline silica, opal, and vitreous silica for frequencies from about 1 to 21 μ. They used a mirror-spectrometer with prisms of fluorite, halite, and sylvite; a Schmidt radiometer; and a Nernst-lamp source, direct comparisons being made with the reflection from a silvered mirror. The results obtained with compact ("dichter") vein quartz, from veins in dolomite in the limestone quarry at Reichenstein, Silesia, are shown in Figure XXXV.5. Quartz of this kind

[6] COBLENTZ, W. W., *Supplementary investigations of infra-red spectra*, Parts V, VI, VII, Carnegie Inst. Washington, Publ. **97** (1908), 183 pp., especially pp. 22, 34.

[7] SCHAEFER, CL., & SCHUBERT, M., *Ultrarotes Reflexionsvermögen von SiO_2*, Zeitschr. Physik (1921) **7**: 313-315.

is usually an intergrowth of crystals of many orientations, and the curve therefore represents an average reflecting power.

The reflecting power of quartz for the near ultra-red spectrum was first measured by Nichols.[8] He used a prism surface perpendicular to the axis, and compared the reflected intensity by means of a radiometer with the reflection from a silvered glass surface, which had previously been shown to be 100 per cent, as nearly as it could be measured, for wave-lengths longer than 4 μ. Comparisons were made at 34 frequencies between $\lambda = 4.50$ and 9.02 μ. The results are shown graphically in Figure XXXV.6.

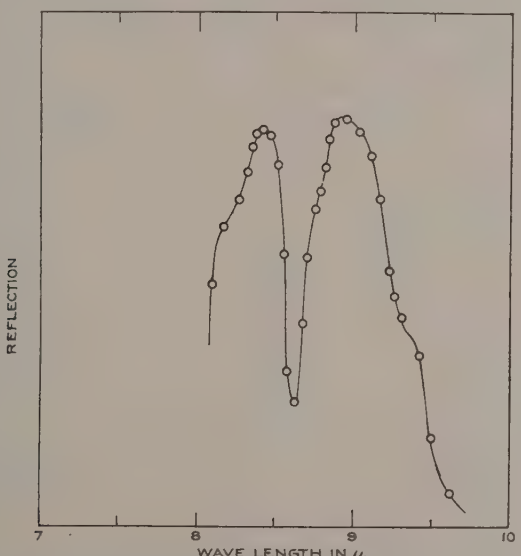


FIG. XXXV.7.—Form of the double maximum near 9 μ in the curve of reflection of quartz, as observed by Trowbridge & Wood, 1899.

The presence of a small proportion of radiation of shorter wave-lengths makes the maxima of reflection appear too low, and the second maximum lower in proportion to the first.

Rosenthal[9] determined the reflecting power of quartz for ultra-red radiation of wave-lengths 8 to 10 μ by measuring the intensity of rays which had undergone three reflections from a quartz surface. The intensity was compared directly, by means of a thermopile, with that from three silvered surfaces. The wave-length was fixed by the angle of refraction of the ray through a

[8] NICHOLS, E. F., Sitzungsb. K. Preuss. Akad. Wiss. Berlin **1896**: 1183-1196; Physical Rev. (1897) **4**: 297-313, 1 pl.; Ann. Phys. u. Chem. (1897) **60**: 401-417, pl. 3.

[9] ROSENTHAL, H., *Ueber die Absorption, Emission und Reflexion von Quarz, Glimmer und Glas*, Ann. Phys. u. Chem. (1899) **68**: 783-800, pl. 6.

rock-salt prism with the help of Rubens' (1892) indices for rock salt, and the position of minimum deviation for sodium light, as a basis. Correction was made for slit width by Runge's formula. The results are contained in Figure XXXV.6.

The data of Rubens & Hertz[10] are also included in this Figure, for comparison.

After Nichols had shown the existence of a strong double band of absorption and reflection by quartz at about 9 μ, Rubens & Nichols[11] developed their method of selective reflection to obtain fairly monochromatic ultra-red radiation in the form of "residual rays" (Reststrahlen). Repeated reflection from a surface eliminates the frequencies which pass through while concentrating

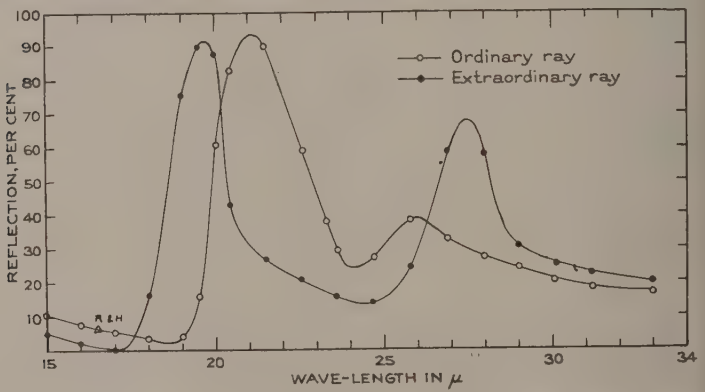


FIG. XXXV.8.—Measured reflecting power of quartz for plane-polarized radiation of wave-lengths 15 to 34 μ. (Liebisch & Rubens, 1919.)

those which are strongly reflected. Repeated reflection from quartz confirmed the existence of maxima of reflection at 8.50 and 9.02 μ, and revealed a further strong reflection at 20.75 μ.

Incidentally to their work on their echelette grating, Trowbridge & Wood[12] examined the form of the first reflection bands of quartz. The echelette grating has about five times as great a resolving power at this frequency as a rock-salt prism, and so permits of a more detailed study of the reflection. Although the absolute percentages were not published, the form of the reflection curve for the pair of bands was given and is reproduced in Figure XXXV.7. The maxima are seen to be nearly equal, with an intervening minimum which has an intensity only about one-third of that of the maxima. It is not clear why the doubling of the second maximum, as found by Reinkober, was not observed by Trowbridge & Wood.

[10] Article cited in note [22]. See also Fig. XXXV.14.
[11] RUBENS, H., & NICHOLS, E. F., Ann. Phys. u. Chem. (1897) **60**: 418-462, pl. 3.
[12] TROWBRIDGE, A., & WOOD, R. W., Phil. Mag. (1910) (6) **20**: 898-901.

The wave-lengths of the maxima were carefully determined, with the following results:

						Mean
First max.	8.42	8.42	8.40	8.36	8.49	8.41 μ
Second max.	8.90	8.99	8.80	8.90	8.90	8.90 μ

The maximum at about 13 μ was not observed by Trowbridge & Wood, probably because, being small, it was wiped out by the threefold reflection which they used.

Reflection of the farther ultra-red by quartz

Information on the reflections beyond 20 μ is furnished mainly by the experiments of Rubens.[13] These were made with the residual heat-rays reflected

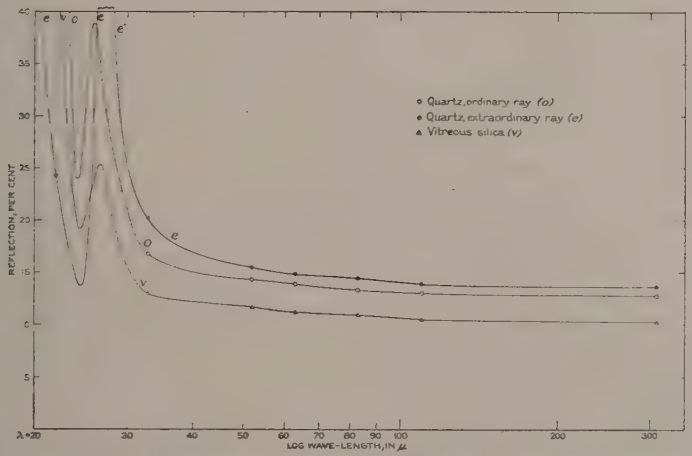


FIG. XXXV.9.—Reflecting power of quartz and vitreous silica for radiation of wave-lengths 20 to 310 μ. (Rubens, 1916.)

by fluorite, aragonite, rock salt, sylvite, potassium bromide, and potassium iodide, these substances giving a range of wave-lengths from 22 to 94 μ. Less homogeneous radiations of about 110 μ and 310 μ were obtained from the heat-radiations of a Welsbach gas mantle, and of the mercury vapor in a vitreous-silica-mercury lamp, respectively.

The reflecting power for natural radiation of plates parallel and perpendicular to the axis was measured, and values for the extraordinary ray were calculated therefrom (see page 700). The material was a crystal from Madagascar.

[13] RUBENS, H., *Ueber Reflexionsvermögen und Dielektrizitätskonstante einiger amorpher Körper,* Sitzungsb. Berlin Akad. 1916: 1280-1293.

This work was supplemented by the experiments of Liebisch & Rubens,[14] in which the radiation was polarized by reflection from a selenium mirror at 68½°, or, for the longer waves, by passage through a diffraction grating of fine platinum wires. The range 15 to 32 μ, for quartz, was examined spectrometrically with measurements at intervals of 0.5 to 1 μ. The radiation was dispersed by a sylvite prism for 15 to 20 μ, and by a grating of silver wire, after reflection from fluorite, for 20 to 32 μ.

The results of Liebisch & Rubens for wave-lengths 15 to 33 μ are represented in Figure XXXV.8.

Rubens' data for the longer wave-lengths are assembled in Table XXXV.2, and plotted in Figure XXXV.9. Those portions of the curves of Figures XXXV.8 and XXXV.11 which come within the range of Figure XXXV.9 are also reproduced, but without indication of the measured points; only the data of Table XXXV.2 are marked by circles or triangles in Figure XXXV.9. It will be seen that Rubens' measurement on quartz at 22 μ lies on the curve of Liebisch & Rubens, but that the corresponding measurement on vitreous silica falls out considerably. No explanation is known for the discrepancy.

The reflecting power of quartz for radiation of wave-length 16.5 μ was determined by Rubens & Hertz[15] as 6.3 per cent. This value is included in Figure XXXV.8 (marked "R. & H.").

TABLE XXXV.2.

REFLECTING POWER OF QUARTZ AND VITREOUS SILICA FOR WAVE-LENGTHS 22 TO 310 μ. RUBENS, 1916; LIEBISCH & RUBENS, 1919.

Source	Wave-length, μ	Quartz *o*	Quartz *e*	Vitreous silica	Chalcedony
Residual rays from CaF_2 through sylvite	22	59.3	24.3	34.0	33.1
Residual rays from CaF_2 and calcite	27.3	...	...	...	24.2
Residual rays from CaF_2 through quartz	33	16.8	20.2	13.0	18.0
Residual rays from NaCl	52	14.5	15.5	11.6	14.2
Residual rays from KCl	63	13.9	14.8	11.1	13.6
Residual rays from KBr	83	13.3	14.4	10.9	12.7
Residual rays from KI	94	...	...	...	12.8
Radiation from Welsbach burner	110	13.0	13.9	10.5	13.0
Radiation from Hg lamp, not purified	...	12.8	13.7	10.3	12.2
Radiation from Hg lamp, purified	310	12.7	13.6	10.2	11.8

The reflecting power of quartz for the residual rays of rock salt and sylvite was determined by Rubens & Aschkinass,[16] with the following results, the

[14] LIEBISCH, T., & RUBENS, H., Sitzungsb. Berlin Akad. 1919: 198-219, 876-900, 3 pls.

[15] p. 265 of article cited in note [22].

[16] RUBENS, H., & ASCHKINASS, E., Ann. Phys. u. Chem. (1898) **65**: 241-256.

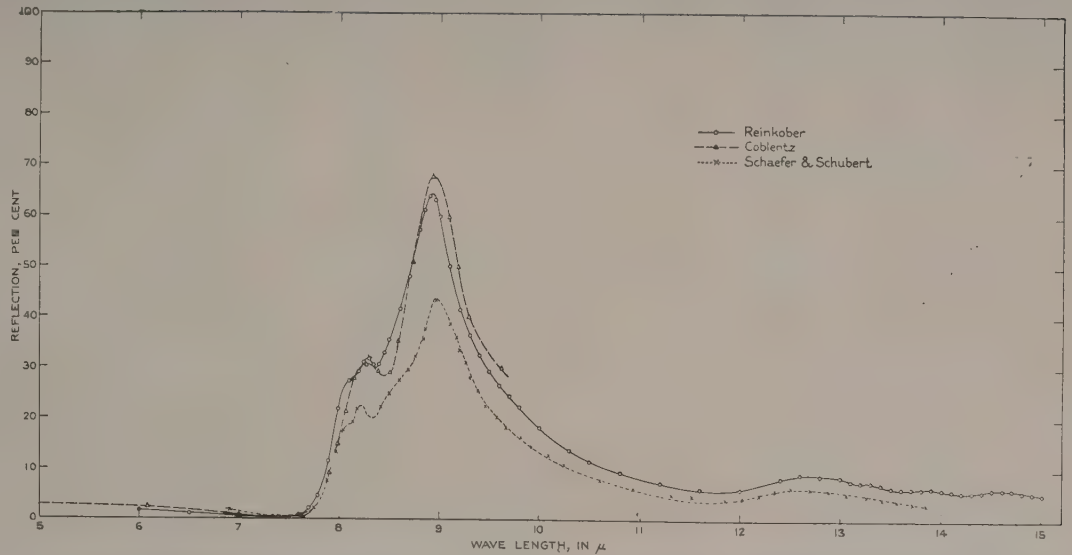


FIG. XXXV.10.—Measured reflecting power of vitreous silica for unpolarized radiation of wave-lengths 6 to 15 μ. (Reinkober, 1910; Coblentz, 1908; Schaefer & Schubert, 1921.)

reflecting power of silver being 100. (The original wave-lengths have been replaced by the later more accurate values of Rubens & Hollnagel[17].)

Radiation	Wave-length μ	Reflecting power
Rock salt	51.7	17.8
Sylvite	63.4	13.0

The first of these points falls considerably above the curve of Figure XXXV.9, the second falls a little below. The radiation was perhaps not sufficiently homogeneous to give an accurate value.

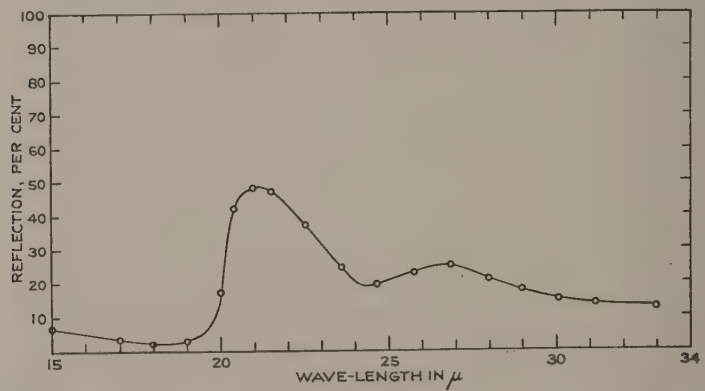


FIG. XXXV.11.—Measured reflecting power of vitreous silica for radiation of wave-lengths 15 to 34 μ. (Liebisch & Rubens, 1919.)

DATA ON VITREOUS SILICA

The ultra-red reflecting power of vitreous silica has been measured in the range 1 to 21 μ by Reinkober, by Coblentz, and by Schaefer & Schubert; and in the range 15 to 300 μ by Rubens and by Liebisch & Rubens. These investigations have all been discussed in connection with the data on quartz, with the exception of some new data published by Coblentz in 1911.[18] The new measurements failed to confirm the existence of a maximum of reflection at 7.8 μ shown in 1908, and due probably to a leakage or other unrecognized error. The measurements[19] were on a block of vitreous silica made by Day & Shepherd (see p. 811).

The first three sets of results on vitreous silica are assembled in Figure XXXV.10. The last two are shown in Figures XXXV.11 and XXXV.9. The

[17] RUBENS, H., & HOLLNAGEL, H., Verh. Deutsch. Phys. Ges. (1910) **12**: 83-98.
[18] COBLENTZ, W. W., Bull. Bur. Standards (1911) 7: pp. 653-655 (Reprint 168).
[19] Information from Dr. COBLENTZ.

Rubens data are included in Table XXXV.2. A discrepancy between the last two at wave-length 22 μ has already been remarked (p. 710).

Data on micro-crystalline silica

The reflecting power of micro-crystalline silica has been measured for the range 1 to 21 μ by Schaefer & Schubert, and for 22 to 310 μ by Liebisch & Rubens.

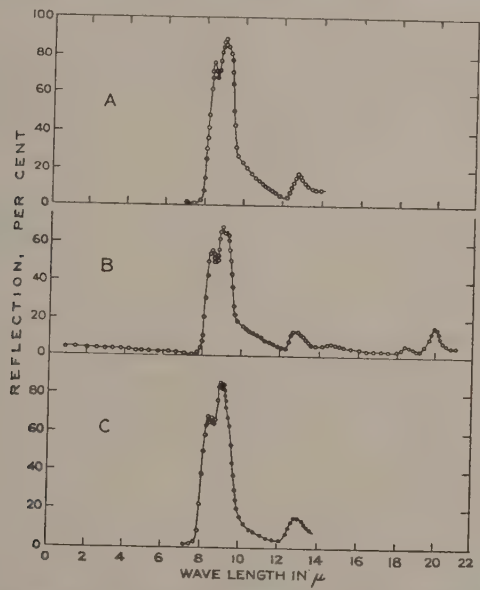


Fig. XXXV.12.—Measured ultra-red reflecting power of micro-crystalline silica: (A) hornstone; (B) chrysoprase; (C) chalcedony. (Schaefer & Schubert, 1921.)

The data of Schaefer & Schubert[20] are shown in Figure XXXV.12. The specimens examined were: (A) Hornstone, also called "white chrysoprase." From Gläsendorf, near Frankenstein, Silesia. (B) Chrysoprase. Dark green specimen, from Frankenstein, Silesia. (C) Chalcedony, finely fibrous. From Island of Nicobar, East Indies.

The three specimens are qualitatively very closely alike in reflecting power, and very similar to clear quartz. Their differences are mainly in intensity of reflection, and may be ascribed to differences in the degree of polish.

The data of Liebisch & Rubens[21] are contained in Table XXXV.2. Their plates were 55 to 60 mm square, and they state concerning the specimen of chalcedony (from Iceland) that no structure was evident to the unaided eye.

[20] Article cited in note [7].
[21] pp. 877-879 of article cited in note [14].

Their results are shown in Figure XXXV.13 in comparison with the curves for the two rays of quartz, reproduced from Figure XXXV.8.

The data on the micro-crystalline forms probably represent an average value for all possible orientations of fibers. The curves for the shorter wave-lengths (1 to 30 μ) resemble the curve of a quartz aggregate, but a difference appears in the longer wave-lengths, in the occurrence of a barely detectable minimum near 80 to 90 μ. A similar, but more marked, minimum is found in the reflection curves of opal and certain silicate glasses.

Wave-lengths of the reflection maxima

In Table XXXV.3 are assembled the wave-lengths for the maxima of reflection by quartz (*o* and *e*) and vitreous silica, as given by various observers. These are quoted from the published data, and represent the observers' own opinions as to the positions of the maxima.

Table XXXV.3.

Wave-Lengths of Maxima of Reflection, as Given by Observers.

Observer	Wave-length in μ							
QUARTZ, ORDINARY RAY								
Nichols (1897)	8.42	...	8.80	...	...	...	...	...
Rubens & Nichols....	8.50	...	9.02	...	...	...	20.75	...
Rosenthal (1899)	8.49	...	9.03	...	...	...	...	...
Coblentz (1906)	8.48	...	9.02	...	12.5	...	...	...
Coblentz (1911)	8.3-8.5	...	9.0-9.2	...	...	...	...	...
Reinkober (1910) ...	8.40 *	...	9.02 †	9.20 ‡	12.52	14.55	...	...
Trowbridge & Wood.	8.41	...	8.90	...	...	...	...	...
Liebisch & Rubens...	...	...	...	...	...	...	21.0	26.0
QUARTZ, EXTRAORDINARY RAY								
Reinkober (1910) ...	8.40 *	8.70	9.02 †	...	12.87	...	...	...
Liebisch & Rubens...	...	...	...	...	...	...	19.7	27.5
VITREOUS SILICA								
Coblentz (1911)	8.3	...	8.95	...	...	...	...	...
Reinkober (1910) ...	8.30	...	8.90	...	12.6	14.6	...	...
Liebisch & Rubens...	...	...	...	...	...	...	21.2	26.8

* Center of mass of two maxima, one at 8.35, and one at 8.50 (weak).
† Center of mass of two maxima, one at 8.90, and one at 9.05.
‡ Weak.

Data on the change of reflection with temperature

Rubens & Hertz[22] determined the effect of low temperatures on the reflection band of quartz at 9 μ. Measurements of reflecting power made at the temperature of liquid air (— 186°C) are compared in Figure XXXV.14 with

[22] Rubens, H., & Hertz, G., Sitzungsb. Berlin Akad. 1912: 256-274.

measurements at room temperature. The effects are extremely small, though measurable. The decrease of temperature of 206° causes the positions of the two maxima to be shifted in the direction of shorter wave-length, to the extent of about 0.02 or 0.03 μ. At the same time the percentage of reflection at the shorter-wave-length maximum is increased a little, while that at the longer wave-length is correspondingly decreased.

A further lowering of temperature to that of liquid hydrogen (— 252°) produced no further significant change. The experimental difficulties of working at this low temperature prevented the attainment of so high a precision as at — 186°, but it can be stated that the change between — 186 and — 252°, if there is any change at all, is probably no greater than between room temperature and — 186°.

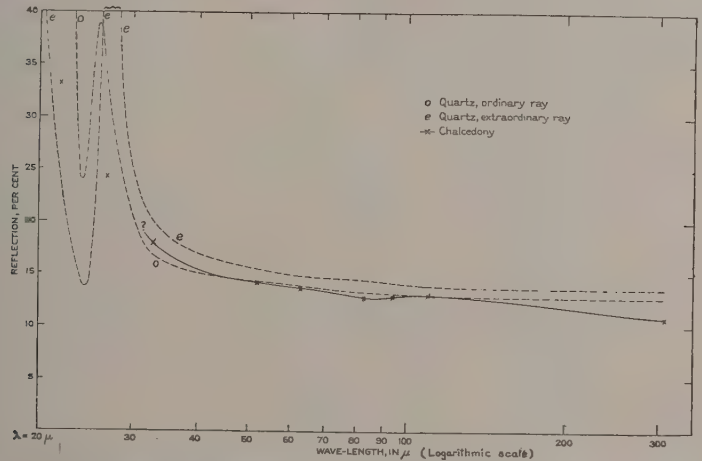


FIG. XXXV.13.—Measured reflecting power of chalcedony, compared with reflecting power of quartz for plane-polarized radiations. (Liebisch & Rubens, 1919.)

No measurements have been made of the reflecting power at higher temperatures. Mügge could observe no variation in the spectral composition or the polarization of light reflected from a polished plane plate of quartz, as the temperature reached and passed the inversion-point at 573°.

Historical note on reflection by silica

The pioneer in research upon the reflection and refraction of the ultra-red was Langley, but the investigator who contributed most to this field of radiometry was Rubens. Beginning about 1890, this work was carried forward by Rubens and his students, or by others using his methods, until now we have a very fair knowledge of the properties of a number of substances, including quartz and vitreous silica, over most of the ultra-red spectrum.

[23] MÜGGE, O., article cited in VII, note [3].

The principal set of reflecting bands in silica, those at 8 to 9 μ, were discovered in 1896 by E. F. Nichols. Rubens & Nichols, by the method of repeated reflection, then found the band at 21 μ. The reflection at 12 to 13 μ was found in 1906 by Coblentz.

Special cases of reflection by silica

Luster

The so-called "luster" of a mineral, one of the diagnostic characters used by mineralogists, is determined by the character of the reflected light and by the visible patterns which reflection makes evident on the surface of the mineral.

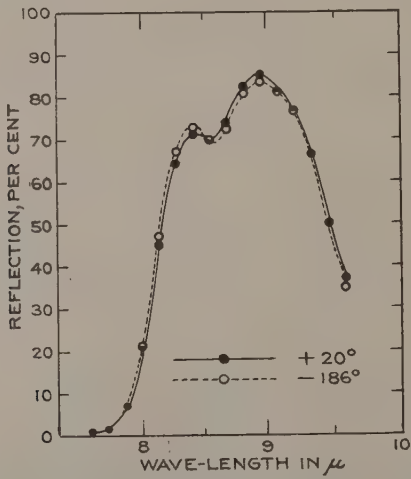


Fig. XXXV.14.—Comparison of the reflecting powers of quartz at 20° and at —186°C. (Rubens & Hertz, 1912.)

The luster of quartz is usually described as "glassy," which means that its surfaces are usually optically smooth and reflect the visible portion of the spectrum without any noticeable selective absorption.

The luster, especially of the conchoidal surfaces of fracture, is sometimes described as "greasy." Undoubtedly there is a difference between "greasy" and "glassy," the former involving perhaps a recognition of scarcely visible undulations on the surface.

A difference in luster between the positive and the negative rhombohedron is sometimes observed on natural quartz crystals, the negative being duller than the positive. This seems to be due to the greater rapidity of etching on the

negative rhombohedron (see p. 508). The crystal under examination, having been exposed to some slightly solvent liquid (perhaps an alkaline water), has had its natural optically smooth negative rhombohedral surfaces dulled by microscopic pits.

According to Ichikawa's numerous observations and experiments on Japanese quartz,[24] primary quartz has a stronger luster than secondary. Ignited quartz (presumably smoky or colored quartz which has been heated to decolorize it) has a stronger luster than before ignition.

Natural etching, probably due to alkaline solutions, gives a stronger luster than artificial etching with hydrofluoric acid. Strong acid yields a stronger luster than weak acid.

Velvety reflection

In 1824 Brewster[25] examined a fractured surface of smoky quartz which had been remarked by a lapidary because of its blackness in reflected light. The effect was not due to a film and was unaffected by solvents. The phenomenon proved to be explainable by assuming a filamentous or velvety surface, the filaments being about 10 mμ long as estimated from the thickness of soap bubble films.

Brewster also noted colors in fractures in amethyst, apparently due to minute points of somewhat greater height. Scott[26] has described iridescence on quartz which may be due to the same cause.

Velvety fractures in twinned transparent quartz were also noted by Haidinger.[27]

[24] Ichikawa, S., article cited in XXV, note [19].
[25] Brewster, D., Edinburgh Journ. Sci. (1824) **1**: 108-110.
[26] Scott, G. S., Amer. Mineralogist (1918) **3**: 183.
[27] Haidinger, W., Edinburgh Journ. Sci. (1824) **1**: 322-333.

Chapter XXXVI. ABSORPTION AND EMISSION

The phenomenon of absorption

If, when radiant energy of a given frequency is being transmitted through a substance, its intensity is measured at any two successive points along its path, this intensity will be found to have decreased between one of these points and the next. Some of the energy has been *absorbed*.

The term "absorption" is sometimes restricted to that part of the vanished radiation which has been converted into thermal energy, but it is difficult to draw a logical distinction between the thermal part and that other portion, usually small but occasionally large, which is being re-radiated as a visible or actinic fluorescence, or is being stored in the form of chemical energy (see XXXVIII). The thermal part is itself re-radiated when the absorbing body becomes heated above its surroundings, and so is not logically separable from the other kinds of re-radiation.

The absorption discussed in the sections on experimental data in this chapter is the total absorption, but the part of it which is not thermal is probably very small in all of the cases studied here.

Quantitative statement of absorption

If the rate of absorption of energy of a given frequency is proportional to its intensity, which is exactly true so far as we know, it follows mathematically that: $J = J_0 e^{-al}$, in which J_0 is the intensity at the first point of observation within the substance, J is the intensity after passing through the thickness l, e is the natural logarithmic base, and a is a constant called the *absorption-modulus*. This is simply the familiar law of compound interest.

The constant a is constant with respect to J and l, but it changes with the frequency. By recognizing radiant energy as a vibration whose intensity depends upon the square of its amplitude, we may take the frequency out of a, and make it a visible part of the formula. Then

$$J = J_0 e^{-\frac{4\pi n\kappa}{\lambda_0} l} \quad \text{or} \quad J = J_0 e^{-\frac{4\pi k}{\lambda_0} l}$$

where n is the refractive index, and λ_0 is the wave-length of the radiation in vacuum; κ is a constant [1] called the *absorption-index*, and k $(= n\kappa)$ is a constant called the *absorption-coefficient*.

As actually measured, the result is always complicated by reflection from surfaces. If J_1 is the intensity in a ray incident on one side of a plate, and J_e is the intensity after emergence from the other side of the plate, the *observed transparency* is J_e/J_1. If R is the proportion reflected at

[1] Sometimes called the "extinction-coefficient," but this term has been used in several different meanings, and may lead to confusion.

each surface, the true or *corrected transparency* is equal to the observed transparency divided by $(1 - R)^2$.

Absorption by silica

Visible

All the mega-crystalline modifications of silica, when pure, are highly transparent to visible radiation. Furthermore, what little absorption exists is essentially the same for all visible frequencies. The forms of silica are therefore *colorless* when seen by transmitted light.

Most substances, even those which are transparent and colorless, become absorbent to certain frequencies in both the ultra-violet and the ultra-red. Silica is no exception to this rule.

Ultra-violet

For ultra-violet frequencies low-quartz is much more transparent than most crystalline substances, glasses, and liquids. In fact, the only material available for construction of optical instruments which excels quartz in its transparency to ultra-violet is fluorite, CaF_2.

Vitreous silica, likewise, is distinguished for its ultra-violet transparency, though it is distinctly less transparent than quartz. The transparency of the other high or low modifications of silica to the ultra-violet is not known.

As soon as the absorption becomes at all appreciable the compound-interest law makes itself felt, and the thickness becomes the important factor in determining how much energy shall get through. For practical purposes it can be stated that the wave-length limit of transmission of the ultra-violet by quartz is 145 mμ for a thickness of 0.2 mm, 150 mμ for 2 mm, and 165 mμ for 20 mm. Therefore quartz lenses and prisms can not be used successfully for radiation of much shorter wave-length than 175 mμ.

Vitreous silica, in thicknesses such as are used in cameras and optical instruments, transmits all the radiation which acts vigorously on ordinary commercial photographic plates, that is, down to a wave-length of 220 mμ, but wave-lengths of 193 mμ and less are almost completely absorbed.

Ultra-red

In the ultra-red spectrum quartz shows decided absorbing power at several frequencies, notably at about 3 μ, 4 μ, 5.3 μ, and between 6 and 7 μ. Strong reflection then follows at about 9 μ, 13 μ, and 21 μ (see XXXV). Vitreous silica absorbs at about the same frequencies as quartz but to a smaller degree.

The transparency of the other high and low modifications to the ultra-red is unknown.

Like refraction and reflection, absorption in a crystalline or an aeolotropic substance changes not only with the frequency, but also (1) with the character of the wave (vibration-direction), and (2) with the direction of the wave with respect to the axes of symmetry of the substance.

Effect of vibration-direction

In any given direction within the substance the ordinary and extraordinary rays in quartz are unequally absorbed, just as they are unequally refracted and reflected. The two curves are, nevertheless, closely similar in general form. See, for example, the absorption of the two rays for wave-lengths of 0.80 to 4.75 μ, as shown graphically in Figure XXXVI.1.

Relation to symmetry

A uniaxial substance in which the absorption of a given vibration differs with the direction in the crystal is called *dichroic*. For ultra-red radiation in the ordinary ray the absorption in quartz is independent of the direction of transmission in the crystal. To the extraordinary ray, on the other hand, it is dichroic. If we could see the ultra-red of wave-lengths 1 to 20 μ, therefore, quartz would not only appear colored in the transmitted radiation, but its color would change as the crystal was turned into various positions.

Effect of temperature on absorption

As the temperature approaches absolute zero the absorption of quartz for frequencies in the ultra-red beyond the absorption and reflection bands approaches zero; that is, the transparency becomes perfect. For frequencies in the region of the ultra-red absorption bands the absorption decreases as the temperature falls, but approaches a finite value at absolute zero.

Above room temperature, the effect of rising temperature is to increase the absorption, but at a diminishing rate.

The behavior of vitreous silica is decidedly different from that of quartz. The absorption of vitreous silica for radiation of wave-length 4.5 μ decreases linearly as the temperature falls, and would approach a finite value at absolute zero if extrapolated downward. The absorption for the long ultra-red of 300 μ is practically independent of temperature, showing a very slight increase as the temperature is lowered from 300 to —186°C.

The experimental data on absorption of ultra-violet

Quartz

The absorption of ultra-violet by quartz has been studied by Pflüger (1904) and by Lyman (1907).

Lyman[2] compared a number of substances with respect to their transparency to ultra-violet radiation from a vacuum tube, dispersing the rays by means of a fluorite prism and observing the intensity on a willemite fluorescent screen in a vacuum. This visual comparison was checked photographically with a large grating spectroscope. The radiation was supplied by a tube containing air at 1 mm pressure, and passed through a fluorite window before traversing the plate under examination. With 8 minutes' exposure and a slit width of 0.09 mm the recorded spectrum transmitted by 0.2 mm thickness of quartz ends at 145 mμ; by 2 mm, at 149 mμ; and by 20 mm, at 162 mμ.

As far as could be determined from examination of 14 specimens of colorless quartz 1 to 2 mm thick, the orientation of the plate with respect to the axis, and the dextro- or levo-rotatory character of the specimen, are without effect on the transparency.

Pflüger[3] observed very considerable differences in the transparency of different specimens of quartz to ultra-violet radiation. The electric spark between metal electrodes served as source for these tests, while the wave-length was measured with a spectrometer and the intensity with a thermopile. Plates 2.6 mm thick, ∥ and ⊥ to the axis, cut from each of four specimens of quartz from different localities, showed the following transparency for radiation of wave-length 186 mμ, uncorrected for reflections:

Specimen	No. 1	No. 2	No. 3	No. 4
Plate ⊥	0.765	0.726	0.51	0.72
Plate ∥	0.76	0.807	0.785	0.745

Number 3 evidently has a high absorbing power and high dichroism. Corrected for reflection, the above data on No. 3 yield the value 88 per cent absorption for a thickness of 10 mm of a plate cut ⊥ to the axis, and 36 per cent for a similar plate ∥ to the axis. A prism cut from this crystal with a 45-degree refracting angle, 4-cm base, and refracting edge ⊥ to the axis, permitted so little of wave-length 186 mμ to pass that it was barely detectable.

As no other optical tests are given by the author, we have no way of knowing whether the large differences noted may be expected in clear homogeneous quartz, or whether they are due merely to scattering by cloudiness or smokiness, and hence are not to be ascribed entirely to true absorption by the silica itself.

The change of absorption with frequency is shown by the following data, based upon measurements by Pflüger on a plane-parallel plate cut perpendicular to the axis and 9 mm thick.

Wave-length in mμ.....	186	203	214	222
Absorption by 1 cm.....	0.328	0.164	0.08	0.058

Vitreous silica

The absorption of ultra-violet by vitreous silica has been studied by Schumann (1903), Pflüger (1904), and Hughes (1914).

Hughes[4] found that a plate of vitreous silica 0.3 to 0.4 mm thick transmits ultra-violet as follows:

[2] Lyman, T., Astrophys. Journ. (1907) **25**: 45-52, pl. 1.
[3] Pflüger, A., Physik. Zeitschr. (1904) **5**: 215-216.
[4] Hughes, A. L., *Photo-electricity* (1914, Cambridge) pp. 137-139.

Wave-length in mμ.....	184.9	197.1	200.2
Transparency	0.24	0.36	0.40

184.9 mμ is the shortest wave-length emitted from a vitreous-silica-mercury arc lamp.

Pflüger [5] observed that a plate of vitreous silica 2.81 mm thick transmitted 56 per cent (uncorrected for reflection) of ultra-violet of wave-length 210 mμ. The absorption of wave-lengths smaller than 200 mμ was practically complete.

Schumann [6] observed that specimens of vitreous silica from different melts varied somewhat in transparency to the ultra-violet. The variation, which was relatively not large, remained unexplained.

The absorptive power of a plate 10.9 mm thick is compared below with that of air for the same frequency, in terms of the time of exposure necessary to obtain equal intensity on a photographic plate:

λ in mμ	199	214	231	257	275	361
SiO_2, seconds	180	20	20	20	20	20
Air, seconds	1–2	11–12	12–13	15–16	16–17	18–19

Experimental data on absorption of the near ultra-red by quartz

The principal sources of information on the near ultra-red (1 to 20 μ) are the experiments of Rubens (1893), Merritt (1895), Nichols (1896), Koenigsberger (1897), Rosenthal (1899) and Coblentz (1906-1915). Nichols covered the range 4 to 8 μ, and Rosenthal went as far as 20 μ but with relatively few measurements. The others worked between the visible and about 5 μ.

The maxima of absorption in the ultra-red, according to various authors, are listed in Table XXXVI.1.

Table XXXVI.1.

Absorption-Maxima of Quartz, as Stated by Various Authors.

Merritt (1895)		Nichols (1896)	Koenigsberger (1897)	Coblentz (1906)
e	*o*			
....	2.9	....	....	2.9
3	....	....	3.05 *	....
....	....	....	3.1 †	....
3.6	....	....	....	....
....	3.75	....	....	....
....	4.1	....	4.05 *	....
....	....	....	....	4.35
....	....	5.02	....	....
....	....	5.3	....	....
....	....	6	....	....
....	....	6.26	....	....
....	....	6.65	....	....

* Smoky quartz.
† Amethyst.

[5] Article just cited.
[6] Herschkowitsch, article cited in V, note [39].

Merritt[7] determined the transparency of quartz to polarized radiation of wave-lengths 0.8 to 4.5 μ. The wave-length was measured with a simple spectrometer with fluorite lenses and prism, followed by a mirror spectrometer,

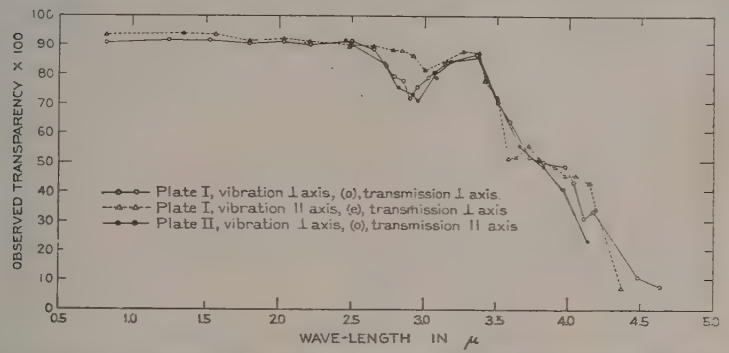

OBSERVED TRANSPARENCY X 100
WAVE-LENGTH IN μ
Plate I, vibration ⊥ axis, (o), transmission ⊥ axis.
Plate I, vibration ∥ axis, (e), transmission ⊥ axis
Plate II, vibration ⊥ axis, (o), transmission ∥ axis

FIG. XXXVI.1.—Observed transparency of quartz to polarized ultra-red radiation. Data of Merritt, 1895.

and the intensity was determined with a bolometer. The radiation was polarized by reflection from a polarizer consisting of four 0.1-mm glass plates.

Measurements were made with a plate 3.02 mm thick, cut parallel to the axis, with vibrations ∥ and ⊥ to the axis. The results are shown graphically

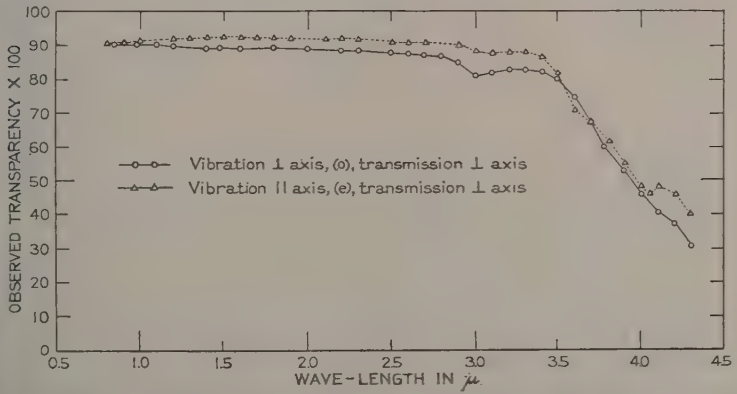


FIG. XXXVI.2.—Observed transparency of quartz to ultra-red. Plate cut parallel to axis, thickness 2.98 mm. Data of Koenigsberger, 1897.

in Figure XXXVI.1. Confirmatory measurements, also shown in the Figure, were made with a plate 3.91 mm thick cut ⊥ to the axis. The curve agrees in form and position with the curve for the vibration ⊥ to the axis in the first ( )

[7] MERRITT, E., *Ueber den Dichroismus von Kalkspath, Quarz und Turmalin für ultrarothe Strahlen,* Ann. Phys. u. Chem. (Wiedemann) (1895) **55**: 49-64.

plate, showing that there is no considerable difference, if any, in the absorption of the ordinary ray with its direction in the crystal.

The method and apparatus used by Koenigsberger[8] were similar to those of Merritt, excepting that Koenigsberger secured a more precise comparison between the absorption of rays vibrating ∥ or ⊥ to the axis by turning through 90 degrees a plate which was cut ∥ to the axis, leaving the apparatus otherwise unchanged. Merritt, on the other hand, made an independent series on each of the two directions. Koenigsberger made observations on colorless quartz, smoky quartz, and amethyst. His results on colorless quartz are shown in Figure XXXVI.2.

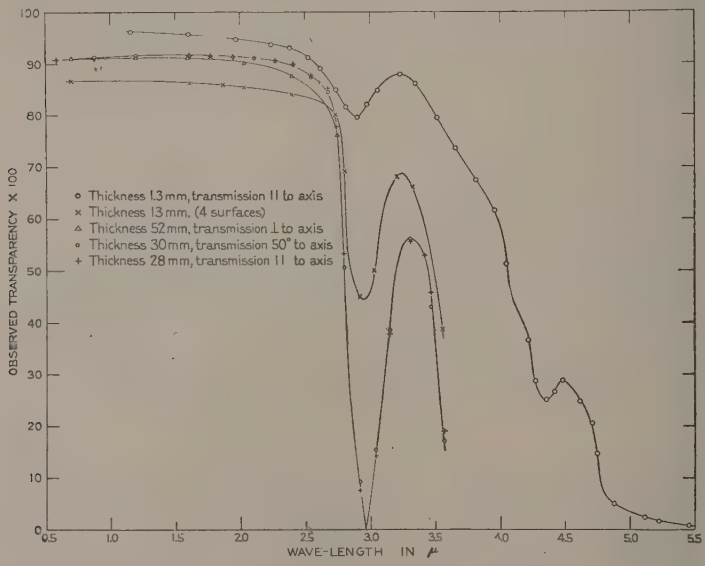

OBSERVED TRANSPARENCY X 100
WAVE-LENGTH IN μ
Thickness 1.3 mm, transmission ∥ to axis
Thickness 1.3 mm. (4 surfaces)
Thickness 5.2 mm, transmission ⊥ to axis
Thickness 3.0 mm, transmission 50° to axis
Thickness 2.8 mm, transmission ∥ to axis

FIG. XXXVI.3.—Observed transparency of various thicknesses of quartz. Data of Coblentz, 1908-1914.

From a comparison of the curves for smoky quartz and amethyst with the curve for colorless quartz, Koenigsberger concluded that the coloring substance in amethyst must be present also in the other two specimens, and must be responsible for the existence of the small absorption maximum at about 3 μ.

Coblentz has made the most extensive investigations of absorption and reflection spectra, so far as number and variety of substances studied is concerned. His range of frequencies lies between the visible spectrum and about 15 μ.

The measurements of wave-length were made with a mirror spectrometer and rock-salt or fluorite prism, with a precision of about 0.02 μ. The intensity

[8] KOENIGSBERGER, J., Ann. Phys. u. Chem. (1897) **61**: 687-704.

was measured by means of a radiometer. The relative precision in readings of intensity was of the order of 0.1 per cent, but the absolute accuracy is probably not better than 1 per cent, in most cases. Differences in the polish of a surface may make several per cent of difference in intensity, without having much effect on the relative precision for a series of frequencies all measured on the same specimen.

Coblentz's results on the observed transparency of quartz are shown in Figure XXXVI.3.

TABLE XXXVI.2.

OBSERVED AND CORRECTED TRANSPARENCY OF QUARTZ FOR ULTRA-RED RADIATION. COBLENTZ, 1914.

Values are multiplied by 100.

Wave length μ	Observed transparency		Corrected transparency	
	Quartz (I)	Quartz (II)	Quartz (I)	Quartz (II)
0.589 3	90.60	90.55	99.29	99.23
0.882 0	91.12	90.70	99.66	99.20
1.197 1	91.45	....	99.91	....
1.613 2	91.38	91.35	99.69	99.66
1.783 5	91.43	91.40	99.67	99.64
1.951 8	91.20	91.26	99.36	99.42
2.112 8	90.92	91.06	98.98	99.14
2.265 4	90.37	90.50	98.31	98.46
2.409 8	89.67	89.79	97.48	97.61
2.545 8	87.20	87.66	94.73	95.22
2.612 0	....	86.26	....	93.67
2.675 7	84.45	85.12	91.68	92.39
2.739 2	....	77.57	....	84.17
2.801 0	50.50	53.19	54.77	57.69
2.921 3	9.17	7.48	9.94	8.11
3.037 3	15.3	14.26	....	15.44
3.150 1	38.4	37.76	....	....
3.313 2	56.0	55.58	....	....
3.419 0	....	52.85	....	....
3.470 0	43.0	45.73	....	....
3.569 0	17.1	18.95	....	....

A set of 8 measurements by Coblentz[9] between 0.8 and 4.6μ, made with a 1-mm plate which was used as a window in a spark tube for the production of emission spectra, are omitted from the Figure, since there are not enough points to give the complete form of the curve. A more complete set, represented in the Figure, was made in 1906,[10] on a plate 1.30 mm thick cut parallel to the axis, and of the optical quality required for polariscope plates.

The next set[11] was made with two plates in series, each 6.5 mm thick. The quadruple reflection accounts for the low values of transmission in the near ultra-red in Figure XXXVI.3. Preliminary values[12] up to 2.8 μ were also obtained with a prism 52 mm thick between its parallel end faces.

[9] p. 45 of publ. cited in XXXV, note [6] (1908).

[10] COBLENTZ, p. 21 of publ. cited in XXXV, note [5].

[11] COBLENTZ, W. W., Bull. Bur. Standards (1913) **9**: 81-117, p. 112 (Reprint No. 181).

[12] COBLENTZ, W. W., *Absorption, reflection, and dispersion constants of quartz*, Bull. Bur. Standards (1915) **11**: 471-481 (Sci. Paper 237, 1914).

Considerably more precise values,[12]—in fact, the best values now available for this range of wave-length,—were obtained on two cylinders: (I) 50 mm in diameter by 29.925 mm thick, with faces at about 40 degrees to the optic axis; and (II) 50 mm in diameter by 27.915 mm thick, with faces plane-parallel to ± 0.5 minute and at a very small angle (49.5 minutes) to the axis. Intensities were measured with a vacuum bolometer.

The observed transparencies of the two cylinders are included in Figure XXXVI.3, and the complete data, including values corrected for reflection, are presented in Table XXXVI.2.

Values of absorption-index (p. 718) calculated from the data of Table XXXVI.2 are given in Table XXXVI.3.

TABLE XXXVI.3.

ABSORPTION-INDEX OF QUARTZ FOR ULTRA-RED. COBLENTZ, 1914.

(Thickness and wave-length in mm)

Wave-length μ	Absorption-index $10^6\kappa$		
	Quartz (I)	Quartz (II)	Mean
1.613 2	0.009	0.010	0.009
1.783 5	0.010	0.012	0.011
1.951 8	0.022	0.021	0.022
2.112 8	0.038	0.035	0.037
2.265 4	0.068	0.066	0.067
2.409 8	0.108	0.109	0.109
2.545 8	0.243	0.235	0.239
2.612 0	....	0.323	0.323
2.675 7	0.410	0.400	0.405
2.739 2	....	0.894	0.894
2.801 0	2.98	2.92	2.95

Quartz (II) was not so highly polished as quartz (I). This would cause more scattering by the surface of (II) and hence should lead to an apparently higher absorption-index. As observed, it is a little the lower of the two. In the opinion of the author the differences are not greater than the possible error of measurement. The data are also in agreement with the somewhat less exact measurements on the 52-mm prism in which the rays, somewhat divergent, were transmitted perpendicular to the axis.

The agreement between the three specimens would seem opposed to the conclusion, already drawn from the work of Merritt and of Koenigsberger that quartz is slightly dichroic between 1 and 4 μ. Nevertheless, such differences as do exist between the two cylinders are in a direction to confirm the differences already found, and if proper allowance could be made for the poorer polish on cylinder II, the distinction would be intensified.

Some early measurements of absorption made by Rubens[13] at 7 frequencies between 0.7 and 3.1 μ need not be given here as they are superseded by later and more complete series.

The measurements just reviewed, made on thicknesses of 1 to 50 mm, have already reached such small values of transparency at 4.5 to 5 μ that even fairly

[13] RUBENS, H., Ann. Phys. u. Chem. (Wied.) (1892) **45**: 238-261.

large relative changes are no longer detectable. The curve is carried farther into the ultra-red by the data of Nichols,[34] who measured the transparency of a thin plate of quartz at 46 frequencies between 4.20 and 8.10 μ. The plate was cut perpendicular to the axis and was only 18 μ in thickness, as computed from its interference bands. The intensity of the direct ray was compared with that of the transmitted ray by means of a radiometer. Figure XXXVI.4 shows the observed transparency.

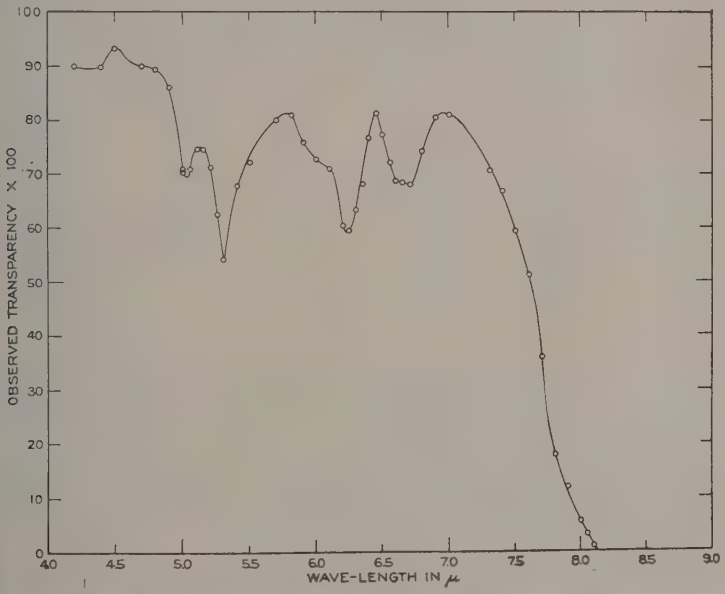


FIG. XXXVI.4.—Observed transparency of a plate of quartz, 18 μ in thickness, perpendicular to the axis. Data of Nichols, 1896.

Values corrected for the observed reflection (see p. 718) are given in Table XXXVI.4, which also contains the values of the square of the absorption-coefficient k (p. 718) calculated therefrom. No energy whatever was transmitted by the plate between wave-lengths 8.1 and 9.0 μ.

Absorption of the farther ultra-red by quartz

For lower frequencies (longer wave-lengths) beyond its reflection-absorption bands quartz again becomes more or less transparent. Measurements in this range have been made principally by Rubens, alone (1911-1913) and in collaboration with Aschkinass (1898), Wood (1910), Hollnagel (1910), Baeyer (1911), and Wartenberg (1914); also by Rosenthal (1899).

[34] Nichols, E. F., article cited in XXXV, note [8].

Rosenthal[15] made a number of measurements of absorption by quartz, but did not publish detailed data. A plate 1 mm thick gave practically total absorption for the entire range 3.5 to 20 μ. A plate 0.1 mm thick was found to be measurably transparent beyond 10 μ, giving a maximum of transparency at 16 μ of 35 per cent. The transparency then falls off rapidly toward the reflection band at 21 μ.

TABLE XXXVI.4.

TRANSPARENCY OF A PLATE OF QUARTZ 18 μ IN THICKNESS, PERPENDICULAR TO THE AXIS, CORRECTED FOR REFLECTION. NICHOLS, 1896.

Wave-length μ	Transparency × 100	k^2 × 10^6	Wave-length μ	Transparency × 100	k^2 × 10^6
4.50	99.0	0	7.30	71.2	121
5.00	75.0	41	7.40	67.4	166
5.30	57.0	174	7.50	60.1	286
5.80	85.4	16	7.60	52.5	466
6.25	61.9	174	7.70	36.9	1149
6.45	83.5	42	7.80	19.3	3215
6.70	69.0	121	7.90	13.9	4747
7.00	82.2	23	8.00	8.01	8136
7.10	80.1	62	8.05	6.43	10240
7.20	76.2	76			

Rubens & Nichols[16] found 15.7 per cent of the residual radiation from CaF_2 ($\lambda = 27.3$ μ) transmitted by a very thin plate of quartz only 18 μ thick; but complete absorption by a thickness of 2.25 mm.

Rubens & Aschkinass[17] measured the transparency of quartz (plates perpendicular to axis) to the residual rays reflected from rock salt and sylvite. A more complete set, including KBr and KI, was made later by Rubens & Hollnagel.[18] The published data are assembled in Table XXXVI.5.

TABLE XXXVI.5.

TRANSPARENCY OF VARIOUS THICKNESSES OF QUARTZ TO ULTRA-RED RADIATION TRANSMITTED || TO AXIS. RUBENS & ASCHKINASS, 1898; RUBENS & HOLLNAGEL, 1910.

Radiation. Residual rays from	Wave-length μ	Observed transparency × 100						Corrected transparency × 100			
		0.50 mm	0.60	2.00	3.03	4.03	5.25	0.60	2.00	3.03	4.03
NaCl	51.7	61*	...	...	...	...	8*	64.2	32.3	23.1	17.4
KCl	63.4	77*	...	...	...	...	18*	85.2	54.0	45.1	30.6
KBr	82.3	...	64.9	47.6	39.2	31.4	...	87.8	64.5	53.2	42.4
KI	96.7	...	...	59.2	...	50.4	...	...	80.0	...	68.0

* Rubens & Aschkinass.

[15] Article cited in XXXV, note [9].
[16] Article cited in XXXV, note [11].
[17] Article cited in XXXV, note [10].
[18] RUBENS, H., & HOLLNAGEL, H., Sitzungsb. K. Pr. Akad. Berlin 1910: 26-52.

Rubens & Wood[19] measured the transparency of quartz for the somewhat inhomogeneous radiation of mean wave-length 110 μ isolated by means of two quartz lenses from the radiation of a Welsbach mantle. The results are contained in Table XXXVI.6. Two values of the absorption-modulus (p. 718) are given. The first, a_1, is calculated from the total thickness and total absorption; the second, a_2, from the increase of thickness and increase of absorption over the measurement just preceding. In both cases the modulus falls off because of the inhomogeneity of the radiation and the more rapid absorption of its shorter wave-lengths. This being the cause of the change, a_2 should fall more rapidly than a_1, as is seen to be the case.

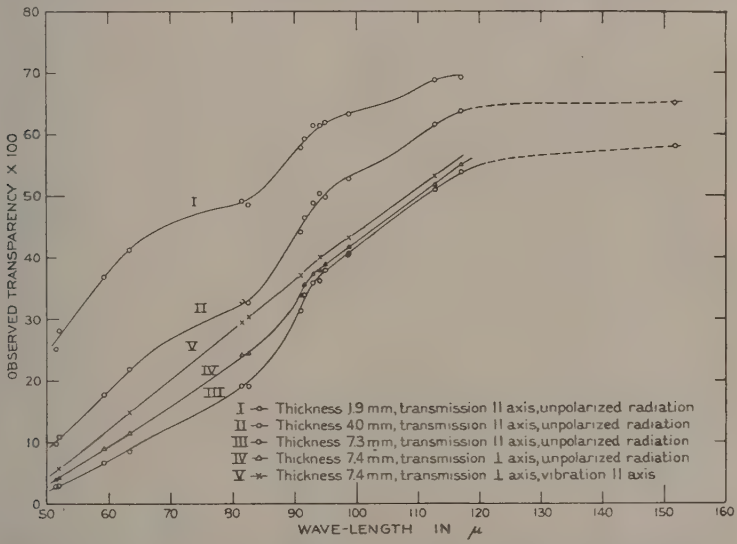

OBSERVED TRANSPARENCY X 100
WAVE-LENGTH IN μ
I
II
III
IV
V
I — Thickness 1.9 mm, transmission ∥ axis, unpolarized radiation
II — Thickness 4.0 mm, transmission ∥ axis, unpolarized radiation
III — Thickness 7.3 mm, transmission ∥ axis, unpolarized radiation
IV — Thickness 7.4 mm, transmission ⊥ axis, unpolarized radiation
V — Thickness 7.4 mm, transmission ⊥ axis, vibration ∥ axis

FIG. XXXVI.5.—Observed transparency of quartz to long ultra-red radiation. Temperature 10 to 12°C. Data of Rubens and of Rubens & Wartenberg.

A better defined and more homogeneous radiation is obtained by repeated reflection from calcite; it has a principal maximum at 93.0 μ and a secondary maximum at 116.1 μ, mean wave-length 98.7 μ. The absorption of this radiation by quartz, as measured by Rubens,[20] is also shown in Table XXXVI.6.

The foregoing data on absorption of the longer ultra-red (beyond 50 μ) by quartz are slightly defective in that the plates were not oriented with exactness perpendicular to the principal axis. The measurements were therefore repeated in connection with a new series of measurements on residual heat rays, made by Rubens[21] and by Rubens & Wartenberg,[22] using carefully cut

[19] RUBENS, H., & WOOD, R. W., Sitzungsb. K. Pr. Akad. Berlin 1910: 1122-1137.
[20] RUBENS, H., Verh. Deut. Physik. Ges. (1911) **13**: 102-110.
[21] RUBENS, H., Sitzungsb. K. Pr. Akad. Berlin 1913: 513-549.
[22] RUBENS, H., & WARTENBERG, H. VON, Sitzungsb. K. Pr. Akad. Berlin, 1914: 169-190.

plane-parallel plates. At the same time a plate parallel to the axis was examined. The radiations used by Rubens differ a little from those previously experimented with, in that the greater part of the path of the reflected rays is in dry air, thus eliminating the disturbing influence of selective absorption by water vapor. This precaution was found unnecessary by Rubens & Wartenberg for the longer wave-lengths of the series.

TABLE XXXVI.6.

TRANSPARENCY AND ABSORPTION-MODULUS OF QUARTZ FOR RADIATION TRANSMITTED ‖ TO AXIS, OF WAVE-LENGTH NEAR 100 μ. RUBENS & WOOD, 1910; RUBENS, 1911.

Values are × 100.

Thickness mm	Corrected transparency		Absorption-modulus		
	Inhomogen-ous radiation $\lambda = 110\ \mu$	Calcite rays $\lambda = 98.7\ \mu$	Inhomog. radiation		Calcite rays
			a_1	a_2	a
2.00	81.3	83.8	0.103	0.100	0.088
4.03	66.4	70.6	0.102	0.089	0.086
7.26	49.8	53.4	0.096	0.075	0.086
11.74	35.5	...	0.088	0.069	...
14.66	29.0	30.2	0.084	0.062	0.082
18.69	22.6	...	0.079		...

The results are assembled in Tables XXXVI.7 and 8, and in Figure XXXVI.5. Table XXXVI.7 contains the observed transparency of three plates cut perpendicular to the axis and one plate parallel to the axis. The values obtained with perpendicular plates hold for unpolarized radiation or for polarized radiation whose vibration-direction is perpendicular to the axis, corresponding to the ordinary ray within the crystal.

The data in the sixth column of Table XXXVI.7 hold for unpolarized radiation, and were determined by taking the means of measurements made with the axis of the quartz first vertical and then horizontal. This is necessary because the repeated reflections by which the residual rays are produced cause elliptical polarization of the resulting rays.

The data in the seventh (last) column of the Table are calculated from those in the fifth and sixth columns. They hold for plane-polarized radiation whose vibration-direction is parallel to the axis, corresponding to the extraordinary ray within the crystal.

Table XXXVI.8 contains the values of the absorption-modulus (p. 718) calculated from the data of Table XXXVI.7 after first correcting for reflections at the two surfaces of the plate with the aid of refractive indices derived from the formula of Rubens & Nichols; the thickness l is in mm.

Two facts are brought out by comparison of the curves in Figure XXXVI.5.

(1) The absorption of plane-polarized radiation vibrating ⊥ to the axis (the ordinary ray) is at all frequencies greater than the absorption of the radiation vibrating ‖ to the axis (the extraordinary ray).

(2) The absorption of the ordinary ray is less regularly variable with the frequency than is the absorption of the extraordinary ray. The dichroism is

TABLE XXXVI.7.

OBSERVED TRANSPARENCY OF QUARTZ TO LONG ULTRA-RED RADIATION. RUBENS, 1913; RUBENS & WARTENBERG, 1914.

Values are × 100. Temperature, 10 to 12° C.

Radiation. Residual rays from	Mean wave-length μ	Plates perpendicular to axis			Plate parallel to axis Thickness 7.393 mm	
		Thickness 1.933 mm	Thickness 3.989 mm	Thickness 7.256 mm	Unpolarized radiation	Vibration ∥ to axis
NH_4Cl *	51.5	25.1	9.83	2.90	4.01	...
NaCl	52.0	28.2	10.9	2.94	4.23	5.70
NH_4Br *	59.3	36.8	17.7	6.56	8.95	...
KCl	63.4	41.1	21.9	8.48	11.5	14.9
AgCl	81.5	49.1	32.8	19.2	24.1	29.4
KBr	82.6	48.5	32.6	19.1	24.4	30.2
$PbCl_2$	91.0	57.8	44.1	31.3	33.9	37.0
TlCl *	91.6	59.2	46.4	33.9	35.6	...
AgCN *	(93)	61.4	48.8	35.8	37.3	...
KI	94.1	61.4	50.3	36.1	37.8	40.0
$HgCl_2$*	(95)	61.8	49.8	37.8	38.8	...
$CaCO_3$	98.7	...	...	40.3	...	...
Hg_2Cl_2	98.8	63.2	52.7	40.5	41.6	43.2
AgBr	112.7	68.7	61.5	50.8	51.7	53.1
TlBr *	117.0	69.2	63.7	53.9	55.0	...
TlI *	151.8	...	65.0	58.0	...	...

* Measurements by Rubens & Wartenberg.

TABLE XXXVI.8.

ABSORPTION-MODULUS a OF QUARTZ FOR LONG ULTRA-RED RADIATION, CALCULATED FROM THE DATA OF TABLE XXXVI.7.

$J = J_0 e^{-al}$. l is in mm.

Radiation. Residual rays from	Mean wave-length μ	Plates perpendicular to axis			Plate parallel to axis Thickness 7.393 mm	
		Thickness 1.933 mm	Thickness 3.989 mm	Thickness 7.256 mm	Unpolarized radiation	Vibration ∥ to axis
NaCl	52.0	0.502	0.480	0.445	0.386	0.346
KCl	63.4	0.310	0.305	0.298	0.252	0.218
AgCl	81.5	0.220	0.207	0.190	0.153	0.126
KBr	82.6	0.227	0.209	0.190	0.152	0.123
$PbCl_2$	91.0	0.138	0.133	0.121	0.107	0.095
KI	94.1	0.107	0.101	0.100	0.093	0.085
$CaCO_3$	98.7	....	....	0.086	....	....
Hg_2Cl_2	98.8	0.092	0.089	0.086	0.080	0.075
AgBr	112.7	0.054	0.053	0.054	0.051	0.048

marked at wave-lengths below 90 μ but nearly disappears for longer wave-lengths.

It is not unlikely that there is a true maximum of absorption for the ordinary ray at about 82 μ. The relative values of transparency for the residual

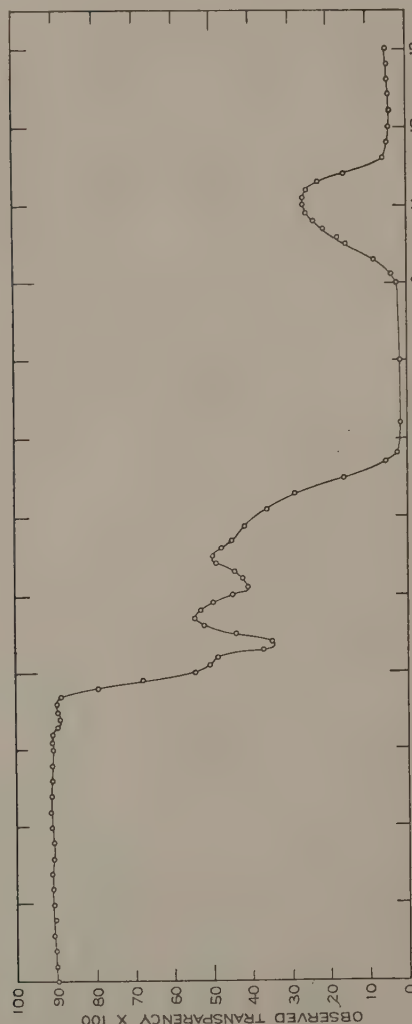


FIG. XXXVI.6.—Observed transparency of vitreous silica, average thickness 0.07 mm. Reinkober, 1910.

rays of AgCl and KBr would indicate this, as their inverted order is not due o experimental error. On the other hand, these residual rays differ in homo- geneity, and the absorption-modulus will therefore change differently with the hickness, especially in a region where the absorption changes rapidly with requency. This inhomogeneity is the principal cause of the variation of a vith thickness, as already seen in Table XXXVI.6.

Rubens & Baeyer [23] discovered a radiation of average wave-length about 00 μ (0.3 mm) emitted by the mercury vapor in a vitreous-silica mercury arc amp. Its absorption by quartz and vitreous silica, compared with the absorp- ion of the 110-μ radiation from a Welsbach mantle, is shown in Table XXXVI.9.

TABLE XXXVI.9.

TRANSMISSION OF LONG WAVE-LENGTHS BY QUARTZ AND VITREOUS SILICA. RUBENS & BAEYER, 1911.

Source of radiation	Transparency × 100		Absorption-modulus
	Quartz, plate ⊥ to axis, 41.7 mm thick	Vitreous silica, 2.00 mm thick	Quartz
Velsbach mantle	12.1	12.5	0.044
Mercury arc lamp.....	25.4	24.2	0.026
Mercury arc lamp, filtered through 2.0 mm of vitreous silica.....	51.8	...	0.0089
Mercury arc lamp, filtered through 0.38 mm of black cardboard.....	58.9	60.0	0.0057

ABSORPTION OF THE VISIBLE AND ULTRA-RED BY VITREOUS SILICA

The absorption of visible light by vitreous silica has been measured by eymans & Allis (1923), and that of the ultra-red by Reinkober (1910), ubens & Wood (1910), and Rubens & Baeyer (1911).

By means of intensity measurements with a Lummer-Brodhun photometer, eymans & Allis [24] obtained the value $a = 0.00696$ for the absorption- odulus of vitreous silica for visible radiation, l being in mm. The corre- onding constant for plate glass is 0.0108; silica is therefore the more trans- rent of the two.

The results of Reinkober [25] on the transparency of thin vitreous silica are own in Figure XXXVI.6. His specimen was a piece of blown silica, vary- g in thickness over an area of 2.5 sq. cm between the limits 0.055 and 0.106 m, with an average of 0.07 mm. The energy transmitted was received on a nsitive thermopile whose galvanometer deflections were compared with those oduced by reflection of the same original radiation from a silvered mirror. The high transparency,—about 90 per cent,—found for wave-lengths up to μ was confirmed by measurements on a plate of vitreous silica 2 mm thick.

[23] RUBENS, H., & BAEYER, O. VON, Sitzungsb. K. Pr. Akad. Berlin 1911: 339-345
[24] pp. 217 and 231 of article cited in XXIII, note [14].
[25] Article cited in XXXV, note [4].

Rubens & Wood found no measurable transmission of radiation of wavelength 110 μ by a plate 3.85 mm thick.

Rubens & Baeyer's data have already been presented in Table XXXVI.9.

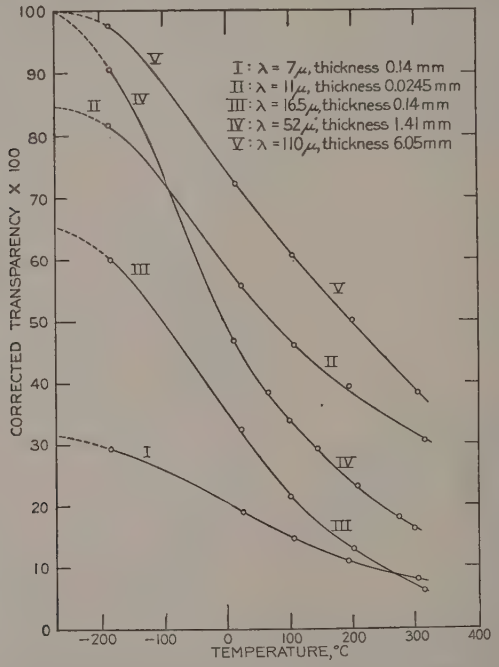


FIG. XXXVI.7.—Transparency, corrected for reflection, of plates of quartz cut perpendicular to the axis. Data of Rubens & Hertz, 1912.

The following data[26] on the transparency of vitreous silica to heat radiations from several sources may be of interest to investigators, though the radiations are not homogeneous.

Source of radiation	Observed transparency of 2 mm vitreous silica (× 100)
Vitreous-silica mercury lamp	32.4
Vitreous-silica amalgam lamp	32.0
Vitreous-silica cadmium lamp	16.4
Vitreous silica heated by Bunsen burner	14.4
Bunsen burner flame	9.4

[26] RUBENS, H., & BAEYER, O. VON, Sitzungsb. K. Pr. Akad. Berlin 1911: 666-67

Experimental data on the effect of temperature on absorption

The most complete piece of work on the effect of temperature on the absorption of quartz in the ultra-red is that of Rubens & Hertz.[27] Their measurements were made at —186° (liquid air) and at 4 to 7 temperatures between room temperature and about 310°C.. Radiations of 4 to 17 μ were obtained from a Nernst lamp and a spectrometer with a rock-salt or fluorite prism.

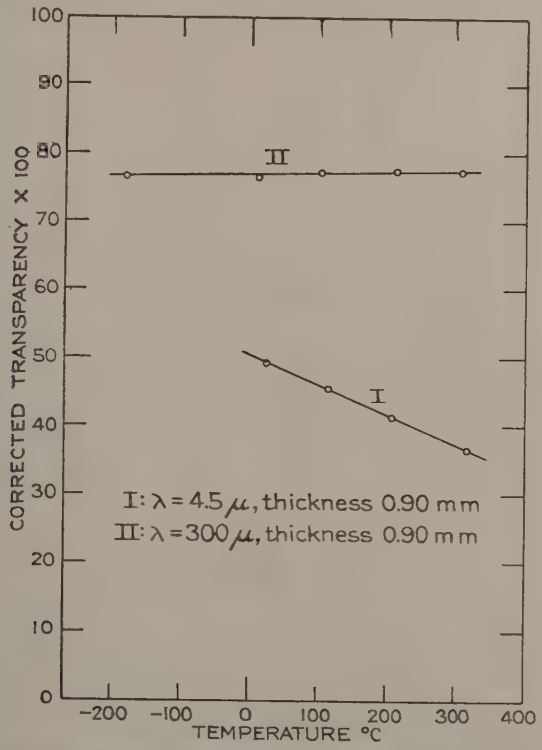


Fig. XXXVI.8.—Transparency, corrected for reflection, of a plate of vitreous silica, as influenced by temperature. Data of Rubens & Hertz, 1912.

Radiation of 52 μ came from repeated reflection by rock salt and filtration through quartz. Radiation of 110 μ came from a Welsbach mantle by way of quartz lenses and filters of quartz and paper, and radiation of 300 μ from a vitreous-silica-mercury lamp.

The results with plates of quartz cut ⊥ to the axis are presented graphically in Figure XXXVI.7, and those with vitreous silica, in Figure XXXVI.8.

[27] Rubens, H., & Hertz, G., Sitzungsb. K. Pr. Akad. Berlin 1912: 256-274.

The absorption-coefficients of quartz for different frequencies and temperatures, as calculated from the data of Rubens & Hertz, are given in Table XXXVI.10.

TABLE XXXVI.10.

ABSORPTION-COEFFICIENT OF QUARTZ AS INFLUENCED BY TEMPERATURE. RUBENS & HERTZ, 1912.

Values are $10^3 k$. $(k = n\kappa.)$

Temp. ° C	$\lambda = 7\ \mu$	$\lambda = 52\ \mu$	$\lambda = 110\ \mu$
— 186	4.93	0.29	0.034
0	6.50	2.10	0.43
100	7.45	3.13	0.71
200	8.81	4.17	1.01
300	9.95	5.35	1.36
$\frac{k_{300}}{k_{-186}} =$	2.0	18.4	40.0

Emission

Every body is constantly emitting radiant energy, whose quality and amount depend primarily upon the temperature of the body.

Like reflection (XXXV) the emission depends to a certain extent upon the character of the surface; but, again like reflection, it depends fundamentally upon a characteristic constant of the substance of which the body is made, namely, its *emissivity*. The emissivity varies with the temperature, and also with the frequency of the radiation whose emissivity is being measured.

QUANTITATIVE MEASURE OF EMISSIVITY

A *black body* is a body which absorbs completely all radiation which falls upon it. It is a consequence of the laws of thermodynamics that at a given temperature both the character and the amount of the radiant energy emitted by a black body are perfectly definite magnitudes, dependent upon no other circumstance than the temperature. The radiation of a black body, therefore, furnishes a convenient standard with which to compare the emissivity of any substance.

Kirchhoff's Law

It is another necessary consequence of the laws of energy that for any given frequency and temperature the ratio between the emission and the absorption of radiant energy by a surface is a constant, equal to the emission of a black body.

Emission by silica

From what has just been said concerning the general principles of emission and absorption, it is evident that the character of the emissivity of silica can be deduced directly from its absorption. A frequency which is selectively absorbed will be selectively emitted; further, if the absorption

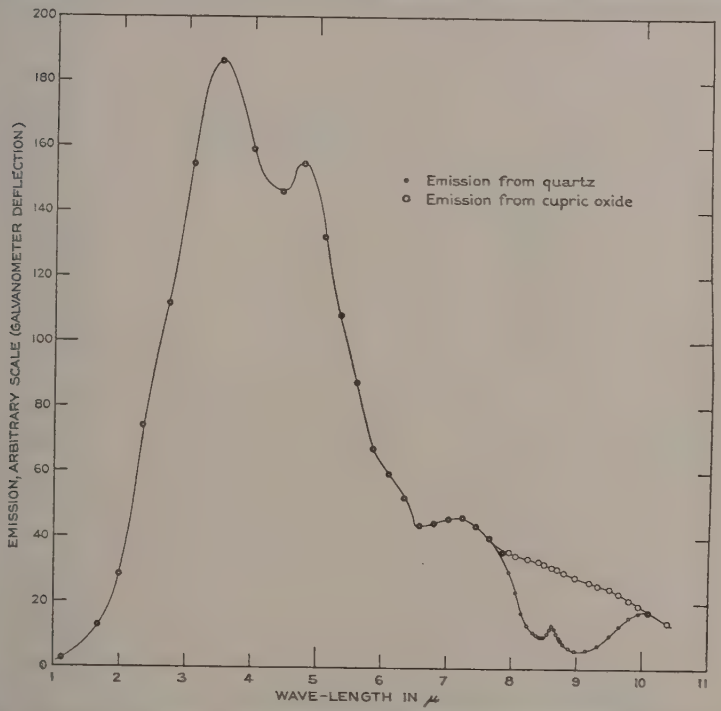


Fig. XXXVI.9.—Emission by quartz at 325°C as compared with that of a black body. Data of Rosenthal, 1899.

of a given frequency increases with the temperature, the emission of that frequency will also increase with the temperature.

The experimental data on emissivity

Quartz

The principal data on quartz are by Rosenthal (1899) and Coblentz (1908).

Rosenthal [28] was the first to make a careful study of its emissivity. Quartz plates were laid horizontal and were heated from below, through the intermediate action of sheets of platinum and copper above a gas burner, to a temperature of 290 to 350°, average 325° C. The intensity of the radiated energy as transmitted through a rock-salt prism and the air of the laboratory was measured with a thermopile. Plates 1 and 2 mm thick gave identical results. Freely suspended plates 4 and 10 mm thick examined by the method of Magnus also gave results at 3.5 μ agreeing with the horizontal plates. The emission

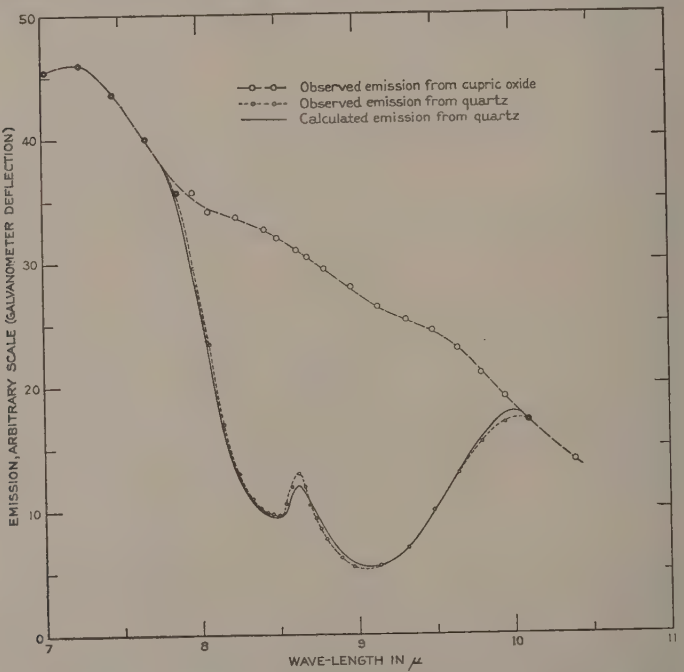


FIG. XXXVI.10.—Comparison of calculated and observed emission by quartz at 325°C.

of the oxidized copper plate upon which the quartz rested, and which radiated practically as a black body, was measured at the same time.

The results, in terms of galvanometer deflections on an arbitrary scale but corrected for slit width, are shown graphically in Figure XXXVI.10. The two curves (quartz and copper oxide) are identical up to about 7.9 μ and show the characteristic absorptions at about 2.7, 4.4, and 5.4 μ which are due to carbon dioxide and water vapor in the atmosphere. At 7.9 μ the reflecting power of

[28] Article cited in XXXV, note [9].

quartz begins to be appreciable. The emission of quartz through its reflecting range is much lower than that of a black body.

The relative emission of the quartz plate (E) can be calculated from the emission of the oxidized copper plate (e) and the reflecting power of quartz (R) by means of Kirchhoff's Law: $E = (1 - R)e$. The result of the calculation, as compared with the observed emission, is shown in Figure XXXVI.10.

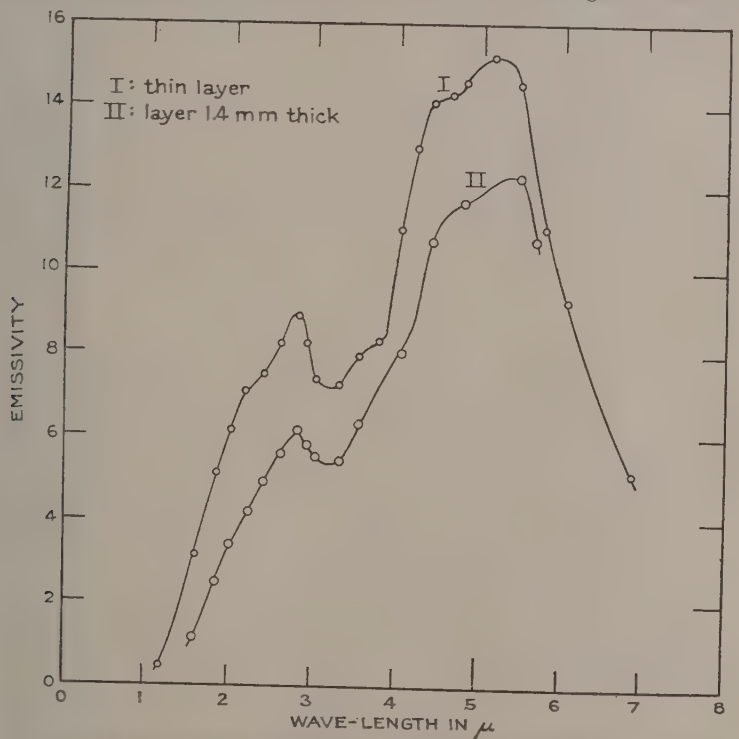


FIG. XXXVI.11.—Emission spectra of quartz. Data of Coblentz, 1908. Temperature about 800°C

The emission spectrum of quartz in the ultra-red has also been examined by Coblentz.[29] The wave-length of the radiation was measured with a mirror spectrometer and fluorite prism, and the intensity with a bolometer. The absorption bands of carbon dioxide and water vapor were eliminated by inclosing the apparatus in a tight box with phosphorus pentoxide powder and potassium hydroxide sticks.

The quartz was used in the form of a fine powder covering the platinum-wire-wound "heater tube" of a Nernst oxide lamp. The temperature could not

[29] COBLENTZ, W. W., pp. 114-115, 140-145 of publication cited in XXXV, note [6].

be measured directly but was at or above 800°C. The results are shown in Figure XXXVI.11 for two thicknesses of the powder. The surface temperature of the thinner layer was estimated at 800°C.

The maxima of selective emission by quartz at 800°C, according to Coblentz, are at 2.2, 2.83, 3.7, 4.4, and 5.3 μ.

In measuring its rotatory power up to about 1500°, Joubert [30] observed that quartz retains its visible transparency at high temperatures, although showing a faint emissive power, such that against a black background it appeared to have a very faint rose tint.

The transparency of vitreous silica for visible radiation persists up to temperatures near the melting temperatures of the crystalline forms. Dufour [31] used this property to demonstrate Kirchhoff's Law. He placed a piece of platinum wire inside of a vitreous silica tube and heated both in a gas flame. The emissive power of the platinum is large, and it glows. The emissive power of the glass is very small, and it accordingly absorbs very little, so that the glowing platinum is visible through the equally hot though invisible glass.

At temperatures where the glass begins to be appreciably soft it loses its transparency and emits light.

Emissivity of aggregates

The emissivity of a substance when in the form of fine grains or powder is not directly deducible from its true emissivity, as measured from a continuous surface. The emissivity of the powder is probably influenced by the shape and arrangement of the grains, and by their distribution as to size. Microscopic or molecular films on the surface of the grains are also likely to have a greater influence than similar films on a continuous surface.

The breaking up of a continuous surface into large grains may increase the emissivity by making the total surface of hills and hollows within a given area greater than before. Further subdivision tends to offset this increase by filling the hollows and tending again toward a smooth surface.

This effect of grain size is shown in the emissivity of quartz sand at 100°C, as measured by Ahr.[32] The emissivity, compared with that of lamp-black as 100, is given in Table XXXVI.11. There is a definite increase as the size of the grains increases from dust up to 2 mm diameter, although the amount of the change can not be very precisely determined.

Table XXXVI.11.

Comparative Emissivity of Quartz Sand at 100° C.

Size of grains, mm	
Less than 0.010	95.1
0.010–0.071	96.5
0.071–0.114	95.9
0.114–0.171	96.1
0.171–0.25	97.9
0.25 –0.50	97.6
0.50 –1.0	98.2
1.0 –2.0	99.5
Mixture, 0.010-2.0	96.7

[30] Article cited in XXXIV, note [24].
[31] J. de Physique (1903) (4) **2**: 498-507.
[32] Ahr, J., Forsch. Gebiete Agrikultur-Physik (1894) **17**: 397-446.

Damp quartz sand is a better radiator of heat than dry sand, probably because water is so opaque to the ultra-red and therefore emits it so efficiently. Ahr [83] publishes the following test of the effect of water on the emissivity at 50°C of quartz sand with grains 0.25 to 0.5 mm in diameter:

Condition	Bolometer reading (arbitrary scale)
Air dry	28.8
With excess of water	30.8
Dampened	29.8
Air dry again	29.0

According to Ahr's comparisons, the emissivity of damp quartz sand at 50 to 100°C is practically as great as that of lamp-black. The emissivity even of dry quartz sand is greater than that of any other soil constituent such as clay, limestone, or humus.

[83] Article just cited.

Chapter XXXVII. THEORETICAL ASPECTS OF THE RADIATIONAL PROPERTIES

The contacts of the radiational properties (XXX) of silica with the general theory of radiant energy on the one hand, and with general and special theories of the structure of matter on the other, are so numerous and varied that this chapter can treat only of a few representative topics.

Refraction and absorption

One of the most important single steps in the advance of our understanding of refraction is due to Drude, who worked out in detail the effects upon radiation of electrons moving periodically in straight and curved paths. This work brought the electromagnetic theory of light and the electron theory of the constitution of matter to the support of a principle which had already been shown by Sellmeier, Maxwell, Ketteler, and Helmholtz to be formally in agreement with the facts of dispersion of refraction; the principle, namely, that the index of refraction of a substance, at any frequency, is controlled by the frequencies of the radiations which are characteristically absorbed or reflected by the substance. If radiant energy progresses in the form of electromagnetic waves, then it must affect the motion of any electrically charged unit met with along its path, whether it be an electron or an ion of complex structure. In particular, if the frequency of the electromagnetic wave happens to be the same as the natural frequency of vibration of the unit, then the energy will either be thrown back (reflection) or appropriated by the charged unit (absorption). If the electromagnetic wave has a very different frequency, its speed through the substance,—and so its index of refraction,—must still be influenced by the natural frequency of the absorbing or reflecting units, even though it progresses without appreciable loss.

Quartz and vitreous silica have absorption or reflection bands both in the ultra-violet and in the ultra-red, and their indices of refraction at any frequency are accordingly determined by the frequencies or wave-lengths of these bands. Leaving out of account those frequencies which are so near the critical values that an appreciable amount of energy is absorbed, we find that the greater part of the curve of refraction against frequency for a transparent substance such as silica should be represented exactly by the so-called Ketteler-Helmholtz dispersion formula:

$$n^2 = K + \frac{M_1}{\lambda^2 - \lambda_1{}^2} + \frac{M_2}{\lambda^2 - \lambda_2{}^2} + \frac{M_3}{\lambda^2 - \lambda_3{}^2} + \cdots$$

where n is the refractive index at wave-length λ; λ_1, λ_2, λ_3, . . . are the constant wave-lengths of the absorption or reflection bands; and K, M_1,

M_2, M_3, . . . are additional constants. Thus if account is taken of only one absorption or reflection band, the relation between n and λ contains 3 constants, while each additional band contributes two additional constants.

The first requirement for a test of the formula is a set of precise measurements of refractive index over a wide range of frequencies. Such data are now available from which formulas for the two indices of quartz and the single index of vitreous silica might be computed, but the computation of the complete formula has been carried out only for the ordinary ray in quartz. It is found that the formula just given will represent the ordinary refractive index N_ω (in air) with great accuracy for the entire range covered by precise measurements, namely 185 to 3000 mμ, with the following constants [1] (λ being expressed in μ):

$K = 4.578\ 77$	$M_1 = 0.010\ 654$	$M_2 = 44.224$	$M_3 = 713.55$
	$\lambda_1 = 0.103\ 087$	$\lambda_2 = 8.85$	$\lambda_3 = 20.75$

These constants were not all drawn directly from the data on refractivity, although they might have been so obtained without reference to any other source. The two ultra-red wave-lengths λ_2 and λ_3 are experimentally determined values taken from the two principal pairs of reflection bands (see Table XXXV.3). λ_2 is the "center of gravity" of the pair at 8.50 and 9.02 μ. λ_3 is the shorter member of the second principal pair, the other member not having been discovered when this set of constants was computed by Rubens & Aschkinass. The formula could doubtless be improved by taking into account the more recent data of Reinkober and others (see XXXV) but this has not yet been tried.

The wave-length λ_1 at about 103 mμ is a computed value, and represents an absorption band in the ultra-violet whose wave-length has not been directly observed, as it is in a region which is difficult of access for laboratory experimentation. There can be little doubt of the real existence of such a band, however,—or possibly of a set of bands having this wave-length as their best representative mean,—for similar but more accessible bands in the absorption spectra of other substances have been found by computation from the refraction-frequency curve and have subsequently been proven experimentally. Furthermore, the rapid increase of absorption in quartz as the wave-length decreases below 180 mμ points to the existence of at least one absorption band in this vicinity.

Another form of the Ketteler-Helmholtz formula, which is mathematically equivalent to that just given, is the following:

$$n^2 = m + \frac{m_1\lambda^2}{\lambda^2 - {\lambda_1}^2} + \frac{m_2\lambda^2}{\lambda^2 - {\lambda_2}^2} + \frac{m_3\lambda^2}{\lambda^2 - {\lambda_3}^2} + \ldots .$$

The new constants are related to those in the other formula thus:

$$K = m + m_1 + m_2 + m_3 + \ldots , \quad M_1 = m_1{\lambda_1}^2, \quad M_2 = m_2{\lambda_2}^2, \text{ etc.}$$

[1] Rubens & Aschkinass, p. 463 of article in XXXI, note [41].

An approximation to the exact formula may be obtained by developing the last one or two terms in series and neglecting the higher powers of λ. The above formula with 7 constants becomes, for example:

$$n^2 = m + \frac{m_1\lambda^2}{\lambda^2 - \lambda_1^2} - k\lambda^2$$

where $k = \frac{m_2}{\lambda_2^2} + \frac{m_3}{\lambda_3^2}$. This formula has only 4 constants instead of 7. The values of the four have been computed by Martens [2] for the two indices of quartz and the index of vitreous silica (absolute indices) and are given in Table XXXVII.1. In the last column I have added the equivalent value of M_1 of the first formula. A later set of values for n_ω computed by Martens [3] is also included.

TABLE XXXVII.1.

	m	m_1	λ_1	k	M_1
Quartz, n_ϵ	1.438 13	0.950 14	0.106 692	0.017 23	0.010 816
Quartz, n_ω (1904).	1.429 19	0.931 73	0.105 805	0.016 35	0.010 430
Quartz, n_ω (1906).	1.400 90	0.956 50	0.104 95	0.010 93	0.010 535
Vitreous, n	1.361 12	0.746 55	0.107 044	0.013 50	0.008 554

The two sets of values of the constants for n_ω differ considerably from each other and from λ_1 and M_1 as used by Rubens, although the fact that the latter apply to N_ω will account for a part of the difference. But, where so many constants enter into the relation, more or less give-and-take is possible among them without causing much distortion of the curve.

REFRACTION AND DIELECTRIC CONSTANT

One of the consequences of the electromagnetic theory of radiation is that the index of refraction of a substance for very long wave-lengths approaches the square root of the dielectric constant: $n^2_\infty = K$. The constant K in the Ketteler-Helmholtz dispersion formula is, then, the dielectric constant of the substance.

TABLE XXXVII.2.

COMPARISON OF REFRACTIVE INDICES WITH DIELECTRIC CONSTANTS.

	n_∞	$\sqrt{K}$
Quartz $\parallel$ to axis.....	2.17	2.15
Quartz $\perp$ to axis.....	2.11	2.12
Vitreous silica	1.95	1.94
Chalcedony	2.05	...

[2] MARTENS & MICHELI, article cited in XXXIV, note [1].

[3] MARTENS, F. F., *Winkelmann's Handbuch d. Physik* (1906, Leipzig) Vol. 6: p. 622.

A comparison of the quantitative data on quartz and vitreous silica shows that this relation is true within the limits of uncertainty of the dielectric constant, which are, however, fairly wide (see XXVI). Table XXXVII.2 compares the indices, as calculated from reflecting power, with $\sqrt{K}$.

Birefringence and its dispersion

The older theories of birefringency ascribed the different variations in this quality to the "crystal molecule" which was supposed to be the fundamental unit in the building up of a crystal. The crystal as a whole could be expected to possess the same peculiarities as its units. The disappearance of this crystal molecule, as a result of modern analysis of the structure of matter and its resolution into atomic nuclei and electrons, has led to the abandonment of the older point of view.

The cause of birefringency as a general phenomenon is evident from what has already been said concerning refraction. The electromagnetic wave progresses by steps from one atom or electron to the next, undergoing a change of phase and a retardation at each step. In an amorphous substance, one in which the atoms are in all possible haphazard positions and orientations, the wave-front averages up to one certain speed regardless of direction. In a crystal, on the other hand, the wave meets with orderly rows and planes of atoms, whose natural vibrations are systematic in character, and whose mutual influence on each other's vibrations is also systematic. If the pattern of arrangement of the atoms is isometric, this mutual influence may not vary with the direction, and so a single wave of constant speed may still be propagated. But if the pattern is not isometric, then it is possible to see how there may be a maximum and a minimum of mutual influence among the vibrations perpendicular to a given direction of propagation, and hence a separation of the wave into two waves of different speed and different states of polarization.

So much for the simple explanation of the phenomenon. When it comes to calculating quantitative values for the birefringence and for its change with frequency the problem is seen to be complex and difficult in any but the simplest of structures. Nevertheless, some regularities can be found with simple assumptions. For example, Havelock,[4] proceeding from the assumption that an isotropic medium is an assemblage of optically isotropic units and not a collection of crystal molecules with their axes distributed equally in all possible directions, has worked out a theory of the dispersion of the birefringence and applied it successfully to the birefringence of quartz. Under the assumption stated, birefringency would be caused by a rearrangement of the isotropic units, either through mechanical stress and electric field intensity, as in artificial birefringency, or by natural arrangement, as in birefringent crystals.

[4] Havelock, T. H., Proc. Roy. Soc. London (1907) A **80**: 28-44.

This is reminiscent of Cauchy's old theory for the dispersion of the refractive index, in which it was assumed that the centro-symmetrical particles are of a size comparable with the wave-length. The variation in index is so wide, however, that Cauchy's theory falls short of providing a complete explanation for dispersion. The variation of birefringence, on the other hand, is relatively small and so this form of theory has a considerably better chance with the dispersion of birefringence than it had with dispersion in general.

On the above-mentioned basis, and following a method of development suggested by Larmor, Havelock shows that, neglecting small second-order terms,

$$\frac{(n_\epsilon - n_\omega)\, n_0}{(n_0^2 - 1)^2} = k$$

where $(n_\epsilon - n_\omega)$ is the birefringence; n_0 is the mean index, $\frac{1}{3}(n_\epsilon + 2n_\omega)$; and k is a constant independent of frequency, at a given temperature.

Applying this equation to Martens' data on the refractive indices of quartz for wave-lengths 185 to 768, and Carvallo's for 801 to 1849 mμ, Havelock found that k is constant within 0.2 per cent (mean value 0.007 245) for the range 358 to 1159 mμ. Above and below these wave-lengths it begins to deviate, in the same direction in both instances, but does not depart more than 1.3 per cent at the farthest from the above-mentioned mean.

A more exact relation which involves no neglect of second-order terms is the following:

$$\frac{1}{n^2_\omega - 1} - \frac{1}{n^2_\epsilon - 1} = k'$$

The constancy of k' over the same range of wave-lengths as that in which the previous k was found constant, is shown in Table XXXVII.3.

TABLE XXXVII.3.

CONSTANCY OF k' IN HAVELOCK'S FORMULA.

λ in mμ	358	434	486	533	560	627	656	768	832	905	991	1097	Mean
$1000\,k'$	14.39	14.39	14.42	14.41	14.42	14.42	14.43	14.39	14.42	14.42	14.40	14.39	14.41

DISPERSION OF THE ROTATORY POWER

Being in effect a refractive constant, the rotatory power of quartz is, like its indices of refraction, dependent upon the wave-lengths of absorption bands in the ultra-red and ultra-violet.

Drude showed that a formula of the form

$$\rho = \frac{k_1}{\lambda^2 - \lambda_1^2} + \frac{k_2}{\lambda^2 - \lambda_2^2} + \cdots$$

would express the measured rotatory powers of many substances. ρ is the rotatory power of the substance for wave-length λ; k_1, k_2, . . . are constants: and λ_1, λ_2, . . . are the wave-lengths corresponding to various free periods of electrons, made evident by absorption bands. The formula for the rotatory power of quartz should therefore contain terms having $\lambda_1^2 = 0.010\,627$; $\lambda_2^2 = 78.22$; $\lambda_3^2 = 430.6$ (see p. 743). λ_2 and λ_3, however, were found to be practically without effect; in other words, k_2 and k_3 are $= 0$. On the other hand, a very high-frequency (short wave-length) term appeared to be needed, whose λ_4 was so small that λ_4^2 was practically zero. This made the formula:

$$\rho = \frac{k_1}{\lambda^2 - \lambda_1^2} + \frac{k_4}{\lambda^2}$$

in which $k_1 = 12.200$; $k_4 = -5.046$

This represented the then existing data on rotatory power with fair accuracy.

To represent his more exact data in the visible region, Lowry found it necessary to re-introduce one of the ultra-red terms which Drude had dropped, making the formula

$$\rho = \frac{k_1}{\lambda^2 - \lambda_1^2} + \frac{k_2}{\lambda^2 - \lambda_2^2} + \frac{k_4}{\lambda^2}$$

in which λ_1 and λ_2 had the same values as before and

$$k_1 = 11.6064;\ k_2 = 13.42;\ k_4 = -4.3685$$

This gives an average deviation for 22 out of 24 wave-lengths in the visible spectrum of only 0.0005 degree. It did not, however, fit the ultra-violet measurements of Lowry, and it was found necessary to introduce independently *two* ultra-violet terms in place of λ_1. Their values are: $\lambda^2_{11} = 0.012\,742$; $\lambda^2_{12} = 0.009\,74$ with the following values for the constants: $k_{11} = 9.5644$; $k_{12} = -2.3114$. At the same time, the very short "zero" wave-length term $\frac{k_4}{\lambda^2}$ is found unnecessary, while the ultra-red term becomes so small that it can be replaced by a constant, $k_5 = -0.1915$, with no λ^2 in the term.

The λ_1 of Drude is evidently a kind of mean value between λ_{11} and λ_{12} of this latest formula. This is the formula which was discussed at page 670 but was there considered simply as an empirical formula.

The foregoing evolution also illustrates how many twists one can give to a formula with plenty of constants in it; and at the same time emphasizes the fact that the process of transmission of radiation through a substance such as quartz, containing perhaps 32 different kinds of electron orbits (see III), is highly complex,—not yet expressible mathematically to the degree of accuracy with which its constants can now be measured.

Effect of temperature on refraction

As the volume of quartz increases with temperature, the indices of refraction should decrease correspondingly. The amount of the change expected per degree, Δn, can be calculated from the linear thermal expansions, and is -14.1×10^{-6} for n_ϵ, and -12.8×10^{-6} for n_ω, for sodium light.[5] The actual changes are in fact negative, as just predicted, but are numerically less than the above values. The true temperature-effect, independent of dilatation, must therefore be positive, and of such a magnitude as to neutralize only in part the negative influence of the dilatation, at least in the visible spectrum.

In the ultra-violet the true positive effect becomes so large as to exceed the negative effect of dilatation.

The positive temperature-effect appears in full force throughout the known curve of vitreous silica, because it has no appreciable thermal dilatation.

The wide range of the data of Martens & Micheli (Tables XXXIV.1 and XXXIV.6) make it possible to estimate the effect of temperature on the constants of the Ketteler-Helmholtz dispersion formula. The effect upon the four constants of the approximate formula (p. 744) is shown in Table XXXVII.4.

It will be seen that the characteristic ultra-violet wave-length λ_1 increases with temperature. This is another way of stating the fact that the temperature-effect on refraction is not due solely to a change in the distances apart of the atoms but represents a specific effect of temperature upon the electron mechanism which is responsible for the ultra-violet band. Furthermore, the change in λ_1 is the same for quartz (both waves) and for vitreous silica. Hence there is a positive temperature-effect which is to be added to the negative effect produced by dilatation in quartz and to the zero effect due to absence of dilatation in vitreous silica, the whole being summarized in the statement that in every case the temperature-effect Δn increases in algebraic value with diminishing wave-length.

Table XXXVII.4.

Effect of Temperature on the Constants of the Approximate Ketteler-Helmholtz Dispersion Formula $n^2 = m + \frac{m_1\lambda^2}{\lambda^2 - \lambda_1^2} - k\lambda^2$.

Martens & Micheli, 1904.

	$10^6\Delta m$	$10^6\Delta m_1$	$10^6\Delta\lambda_1$ in μ	Δk
Quartz, n_ϵ	67.838	— 80.195	6.3200	0
Quartz, n_ω	69.390	— 80.048	6.3200	0
Vitreous silica	69.400	— 41.832	6.3200	0

[5] Pockels, F., p. 305 of article cited in XXXIX, note [20].

Significance of ultra-red reflection

Reference was made in Chapter III to two contrasted modes of combination of atoms: one brought about by the sharing of electrons between two atoms; the other, by the transfer of one or more electrons from one atom over to the other, making a positive ion and a negative ion out of the two atoms.

The phenomena of the residual rays or characteristic reflection bands of silica (XXXV) indicate the presence in the substance of charged ions. The vibration-frequencies corresponding to the wave-lengths λ_2 and λ_3 are relatively slow, and of a magnitude such that the vibrating units must be masses of the order of size of silicon and oxygen atoms, or groups of such atoms. These can be acted on by the electromagnetic wave only if they are electrically charged. The phenomena are therefore qualitatively in agreement with the hypothesis that the combination of silicon and oxygen in the solid modifications is due, at least in part, to the transfer of electrons and the formation of silicon and oxygen ions. The quantitative explanation is not yet clear, for silica has more reflection bands than were to be expected from simple assumptions regarding its constitution.

Significance of the temperature-coefficients of birefringence and rotatory power

The existence of ultra-red reflections points to the existence of ions of atomic and molecular size. Other radiational properties are not explainable by ions alone.

Some calculations on this matter have been made by Perrier,[6] whose work is not yet, however, available in detail. Perrier shows that if we assume only the dissymmetry of polarizability which is due to an electrostatic molecular field, the birefringence due to orientation should *increase* with temperature. On the other hand, if we assume only permanent dipoles,[7] with the dissymmetry of polarization giving rise to subordinate couples, then the birefringence should *decrease* linearly with temperature.

The changes actually observed conform to neither of the above simple assumptions, and are explained in the following manner:

The rotatory power is assumed to be due to lamellae arranged helicoidally. These lamellae owe a part of their birefringence to a spontaneous polarization in a direction lying in the plane of the lamella, perpendicular to the vertical axis of the quartz. The other part of the birefringence corresponds to an axis perpendicular to the first, but still in the plane of the lamella. The retardations are additive for a ray in the plane, but are

[6] Abstract cited in XXXIV, note [37].

[7] A molecule formed by sharing of electrons between unlike atoms can hardly have the properties of a neutral object; it must be considered as reacting toward external influences like an electric "dipole."

in opposition for a ray parallel to the axis. With rising temperature the spontaneous polarization gradually disappears; the removal of its additive effect in the horizontal plane causes the decrease of the birefringence, while the simultaneous removal of its negative effect in the vertical direction causes the increase of the rotatory power. The influence of the spontaneous polarization having disappeared completely at the inversion-point (573°), any further increase of temperature brings out the normal effects, namely, an increase in both birefringence and rotatory power but at a slower rate than before.

The non-linear decrease of the birefringence below the inversion-point is ascribed provisionally by Perrier to the variation of the molecular field accompanying thermal dilatation.

Isotope effects

The isotopes of an element (see p. 23) differ in mass; they should therefore differ in their characteristic vibrations, and by amounts which can be calculated. Plyler and others have recently been examining the ultra-red spectra of salts containing isotopous elements such as potassium and bromine, and have found small irregularities in the reflection and transmission curves which can be interpreted as due to the subordinate isotopes. Silicon consists mainly of Si^{28} (see p. 24) but contains also small amounts of Si^{29} and Si^{30}. There should be corresponding irregularities on the curves. The experimental curves are certainly irregular enough (see Chapters XXXV and XXXVI) but the differences between experimenters are such that the whole region from 5 to 30 μ may have to be gone over again more carefully before the influence of the small percentages of the isotopes can be established. If and when the effect is established, it will be possible to say more definitely which atoms are active in producing the characteristic reflections.

General comment

It is evident that even now sufficient experimental data are available to permit of a considerable advance in the interpretation of the radiational properties of quartz and vitreous silica in terms of their structure. The next step would seem to be the definite placing of the electron orbits which influence radiation, and the deduction therefrom of the constants of refraction, birefringence, and rotation and their change with temperature. As our knowledge of the crystalline state and of the relation of electron motions to radiation is now advancing rapidly, we may hope that the complete and detailed explanation of all these properties will not be long delayed.

Chapter XXXVIII. SCATTERING AND RE-RADIATION

Scattering

Although most of the vanished radiational energy of a ray passing through a substance may be assumed to have been lost by absorption (Chapter XXXVI) there is always the possibility that a part of it has been diverted through *scattering,* which is the shunting off of portions of the radiation at all angles to the incident ray. This scattering becomes very large in a so-called "cloudy" material, that is, a material containing many particles whose diameter is comparable with the wave-length of the radiation, and whose index of refraction is different from that of the substance itself. In such a case the scattered radiation renders the track of a beam of light visible from any direction. Scattering due to small particles, including molecules, is nearly the whole cause of the brightness of the sky except when it is more or less clouded, and is the cause, in large measure, of the visibility of a sunbeam.

Scattering by silica

It is to be expected that cloudy or smoky quartz, which contains a multitude of very small inclusions, will scatter visible light. But scattering is also observed even in quartz which is optically clear. It is then not so easy to see as in cloudy quartz, but with proper experimental arrangements it can be demonstrated visually and can easily be photographed.

Silicate glasses show a scattering power comparable with that of liquids, and vitreous silica may therefore be expected to have a visible scattering power greater than that of quartz, but quantitative measurements have not been made.

Tridymite and cristobalite have not been examined.

The relative intensity of the scattered radiation from quartz, as determined photographically and compared with several other substances, is as follows:[1]

Dust-free air	1
Clear quartz	8
Pure water[2]	158
Plate glass	300
Liquid ether (minimum)	900

[1] Strutt, R. J. [Rayleigh, IV], *Scattering of light by solid substances,* Proc. Roy. Soc. London (1919) A **95**: 476-479, pl. 12.

[2] Raman, C. V., p. 49 of work cited in note [4].

The experimental data on scattering by silica

Most of the observations on scattering by quartz have been made by Strutt (Lord Rayleigh, IV) and by Raman.

Strutt[3] seems to have been the first to observe scattering in optically clear solids such as glass, although, as he himself remarks, the effect is so easy to obtain that it must have been observed before.

In clear quartz, Strutt could show the scattering only photographically, but Raman[4] has succeeded in demonstrating it visually, in the following manner. A block of quartz with smooth polished faces is immersed in a tank of clean distilled water, in order to minimize surface reflections. A converging lens is used to bring a beam of sunlight to a focus within the block. The blue track of the beam within the block may then be readily observed, and its intensity can be judged by comparison with the scattering in saturated ether vapor.

Strutt states that he found differences in scattering power among specimens of quartz which appeared equally clear, but the relative magnitudes have not been published.

Polarization of the scattered light

Scattered radiation is always partly or wholly polarized. Most of the radiation coming off $\perp$ to the original beam is polarized with its direction of vibration in the plane $\perp$ to the beam, but there is also a second smaller portion which is not polarized. The relative intensities of these two kinds of radiation may be used to obtain important indications concerning the constitution of the substance.

The light scattered by clear quartz is almost completely plane-polarized in the normal way, as shown by the formation of only one image when a double-image prism is placed in front of the observing camera. In the much more intense scattered radiation given by a yellow quartz from Madagascar, unpolarized light is also present, showing itself by the formation of a second though much weaker image when examined through the double-image prism. Strutt found that the weak image (vibrations $\parallel$ to original beam) had only 0.7 per cent of the intensity of the strong image. In a slightly smoky Brazilian quartz the proportion was 3 per cent. Sur[5] found the proportion to be 5.7 per cent in a specimen of smoky quartz. Raman[6] reports incomplete polarization of the light scattered $\perp$ to the axis in clear quartz, with the primary beam also $\perp$ to the axis.

The effects are best observed when the original beam is sent along the optic axis and is viewed $\perp$ thereto. Under other circumstances the birefringence may affect the relative intensities more than does the polarization by scattering.

[3] Strutt, R. J., article just cited.
[4] Raman, C. V., *Molecular diffraction of light* (1922, Calcutta), p. 81.
[5] Sur, N. K., Proc. Indian Assoc. Cultiv. Sci. (1923) **8**: 271-275.
[6] Raman, C. V., p. 82 of work cited.

Some optical effects of scattering in quartz

Some interesting effects of scattering were obtained by Strutt[7] with smoky quartz.

When unpolarized white light is used, with the original beam $\perp$ to the optic axis, the scattered light is subject to dispersion by rotation, being viewed along the axis, and the two polarized beams transmitted by a double-image prism after they have passed through a considerable thickness of quartz therefore appear of about equal intensity.

If plane-polarized white light is sent along the axis, the scattering particles act as analyzer, and since the plane of polarization is rotated proportionately to the distance traversed, the result is a series of colored spectrum bands which lose purity after a few repetitions because of superposition. With plane-polarized monochromatic light sharp bands are obtained, decreasing in intensity through absorption, but not decreasing in purity.

If now plane-polarized white light is transmitted axially through a piece of dextro-quartz and a piece of levo-quartz in series, the result is first a loss of purity of color in the bands followed by complete restoration of their purity because of the reversal of the rotational effects in the second crystal.

Theory of scattering in silica

Theory for the liquid and glass

Strutt assumed that the scattering power of silicate glasses and of clear quartz is due to submicroscopic invisible inclusions. He was led to this belief by the large variations in scattering power shown by different specimens of a given material.

This was a reasonable deduction, but it has proved to be unnecessary, for it can be shown theoretically that any liquid or solid substance in which the atoms or atom-groups are in a state of thermal vibration should exhibit scattering of light. The variations observed by Strutt may therefore be regarded as chance variations superposed upon a phenomenon which is generally observable.

The thermal agitation of the molecules of a liquid must result in irregular and evanescent variations of density throughout the liquid, and these variations will result in a scattering of light. If the effect is due simply to the crowding or thinning of molecules by thermal agitation and is unaffected by any chemical attractions among them, the amount of scattering can be calculated in terms of the compressibility and refractive index of the liquid. By applying Boltzmann's entropy-probability principle and the electromagnetic equations, Einstein,[8] following Smoluchowski,[9] developed formulas from which it follows that the relative intensity of light scattered at right angles to the incident beam by 1 cc of liquid is

[7] Article cited.
[8] Einstein, A., Ann. Physik (1910) (4) **33**: 1275-1298.
[9] Smoluchowski, M. v., Ann. Physik (1908) (4) **25**: 205-226.

$$\frac{\pi^2}{18}\,\frac{RT\beta}{N\lambda^4}\,(n^2-1)^2\,(n^2+2)^2$$

where R is the gas constant, T is the absolute temperature, β is the coefficient of compressibility of the liquid, N is the number of molecules in a gram-molecular weight, λ is the wave-length of the radiation, and n is the index of refraction of the liquid.

For ideal or nearly ideal gases the formula reduces to Rayleigh's standard formula for scattering, while in its unchanged form it agrees quite well with the data for certain liquids. The formula thus brings under one law a wide range of conditions under which scattering is observed.

Let us assume for the moment that the formula holds for liquid silica or a liquid silicate mixture at a high temperature. If the liquid is rapidly cooled, its solidification into a glass fixes permanently some of the density variations, and a part of the scattering power of the liquid becomes thereby fossilized, so to speak, in the glassy state. Experiments by Strutt and by Raman show that the scattering power of certain optically clear glasses is in fact 300 to 600 times that of dust-free air, or two to four times that of water and 40 to 80 times that of crystalline quartz.

The facts are thus in qualitative agreement with the theory. Quantitative comparison could be made only if we knew the compressibility and refractive index of the liquid silicate.

Theory for the crystalline modifications

Thermal agitation of atoms also goes on in a crystalline solid, as well as in a liquid. Hence there should be some scattering of light even by a clear crystal,[10] because of the minute and evanescent variations of density occurring within it, although the relative fixedness of its atoms precludes its scattering anywhere near as much light as a liquid or a very dense gas. As we have seen, clear quartz does scatter light, but with far less intensity than clear water.

If it could be assumed that the principle of equipartition of energy is applicable to a crystalline solid as well as to a liquid, then the Einstein-Smoluchowski formula already referred to might be used to calculate the amount of scattering. The heat-content of solids, however, is less than that corresponding to the principle of equipartition (see XIX). The scattering-coefficient obtained from the formula is therefore too high. Raman,[11] by assuming that the coefficient is less than the "theoretical" by an amount proportional to the deviation of the heat-content from the "theoretical," estimated that quartz should scatter light about 10 times as strongly as dust-free air at atmospheric temperature and pressure. This is about the amount found photographically by Strutt (see p. 751).

[10] Larmor, J., Phil. Mag. (1919) (6) **37**: 161-163.
[11] Raman, C. V., Nature (1922) **109**: 42.

Theory of the incomplete polarization

According to the Rayleigh theory for scattering by a gas, if the molecules are spheres the scattered light in a direction perpendicular to the primary beam should be completely polarized. But if the molecules do not have spherical symmetry then a certain proportion of unpolarized light should be found, and this is what is actually observed experimentally. Cabannes [12] derived the following correction factor by which the intensity is to be multiplied: $\frac{6(1+r)}{6-7r}$, in which r is the ratio of the weaker to the stronger component; this brings the data on intensity in gases into accord with the theory.

Correspondingly, light scattered $\perp$ to the primary beam by a liquid, in accordance with the Einstein-Smoluchowski theory, would also be completely polarized. The polarization actually observed is not complete and the intensity not that predicted, but when the Cabannes correction is applied to the formula for certain liquids the observed value is approached much more closely. Just what this means in terms of the structure of the liquid is not as clear as for the gases, but there are evidently possibilities of obtaining information about the positions and shapes of atom-groups from the degree of the polarization.

Effect of temperature

Raman [13] assumes that the change of the intensity of the polarized fraction with temperature may be accounted for entirely by the Einstein-Smoluchowski theory, but that the change of the unpolarized is proportional to the number of molecules per unit volume. This has worked out well for gases, liquids, and liquid mixtures and may prove applicable to the question of polymerization of silica.

Effect of frequency

Raman & Rao,[14] working with organic liquids, have found that the proportion of unpolarized light, due to anisotropic atom-groups, is a function of the frequency of the incident light. This indicates that the anisotropy is due to difference of optical frequency in the group in different directions. Here, again, is a possible way of finding whether vitreous silica and solutions of colloidal silica have a thread structure or contain silica threads, as assumed in the theory presented in Chapter XV. Particularly interesting results should be obtainable from silica rods, if drawing has influenced the orientation of the threads (see p. 270).

[12] Cabannes, J., Ann. de Physique (1921) **15**: 5-150.
[13] Raman, C. V., Nature (1922) **110**: 11.
[14] Raman, C. V., Nature (1922) **110**: 77-78.

Scattering of light originally polarized

There is still another line of evidence which may give information on the structure of silica. Suppose the primary beam, instead of being the unpolarized light ordinarily used in such experiments, to be *plane-polarized,* then the light scattered by a gas or a liquid, in which the molecules are not oriented in any regular way, is still only partially polarized, just as before. But the light scattered under similar circumstances by a crystal, in which the atoms are in fixed positions and orientations from which they move only by thermal vibration, should remain polarized. This has been found by Raman [15] to be true of quartz.

If the process of transformation of vitreous silica into cristobalite consists in a gradual orienting and relocating of the atoms, as assumed in the theory of silica already presented (XV), then the progress of the action with repeated heatings at 800 to 1100° should be evidenced by a gradual decrease in the proportion of unpolarized light scattered when the primary beam is plane-polarized. Whether the total intensity would decrease at the same time is more in doubt.

Luminescence

Types of luminescence

Luminescence is the general name given to the phenomenon exhibited by some substances of emitting visible radiation which is due to some other cause than the temperature. Of the various kinds of luminescence, distinguished according to their exciting causes, the following have been most frequently observed:

Tribo-luminescence: produced by pressure, friction, or mechanical shock.
Photo-luminescence or fluorescence: produced by absorbed radiation.
Cathodo-luminescence: produced by electron bombardment.
Flame-luminescence: produced by exposing the substance to a flame.
Thermo-luminescence: apparently produced, like ordinary visible emission, by high temperatures, but exhibiting a distribution of intensities differing from that of a black-body radiator.

The luminescence sometimes persists for a while after the exciting cause has ceased to act. This persistent luminescence is often called *phosphorescence.*[16] We may thus have tribo-phosphorescence, photo-phosphorescence, etc.

The luminescence, though diminishing or disappearing with or soon after the removal of the excitation, may be revived at some later time

[15] Raman, C. V., p. 83 of work cited in note [4].
[16] Called "secondary phosphorescence" by Beilby (*Aggregation and flow of solids* 1921).

usually by an increase of temperature. This effect is known as *revived phosphorescence.*

Allied to revived phosphorescence is the *pyro-luminescence* which appears in some minerals, including quartz, on heating. It can not strictly be called revived phosphorescence because the original source of the energy which has been stored and which is released by the heating is not always known with certainty.

Tribo-luminescence in silica

Quartz, vitreous silica, and the natural micro-crystalline varieties all exhibit *tribo-luminescence,* which is the name given to the light produced when a fragment is struck, scratched, or broken. The data are rather fragmentary and are almost entirely qualitative. Observations of recent date are mentioned below.

Observations on quartz

When two quartz crystals are struck together by their prism edges, both emit a luminescence. Amethyst and milky quartz show this phenomenon, but smoky quartz and cairngorm do not. They gain the property, however, after their color has been destroyed by heating.[17]

When quartz is cleaved parallel to the second-order prism $\{11\bar{2}0\}$ the tribo-luminescence is stronger than when it is cleaved in other directions.[17]

1-cm quartz cubes (St. Gothard), which crushed explosively in a testing-machine at a maximum pressure of 15000 megabaryes, showed brilliant green luminescence, easily visible in daylight, when they collapsed.[18]

The friction of a quartz crystal against quartz sand on a rotating disk yields a bright yellow luminescence,[19] of duration less than 0.01 second, to judge from the data on other substances.

Vitreous silica

Tribo-luminescence in vitreous silica was first observed by Gaudin[20] in 1839, when he noticed that there is a flash of light when a bead of fused quartz, chilled in water, is broken with a hammer.

Beals[21] has examined the quality of the light given off by the friction of two pieces of the silky or satin-finish variety of vitreous silica tubing, one of which was mounted on the shaft of a slow-speed emery-wheel motor. This tubing gave more intense tribo-luminescence than quartz crystals. The light was photographed, with exposures of 15 to 90 minutes, in a quartz spectrograph. The spectrum is continuous with no lines, and extends over the visible region and a short distance into the ultra-violet.

[17] Ichikawa, S., article cited in XXV, note [39].
[18] Rinne, F., article cited in XXIV, note [26].
[19] Levison, W. G., Science (1904) **19**: 826-827.
[20] Article cited in VI, note [25].
[21] Beals, C. S., *On some triboluminescence spectra,* Trans. Roy. Soc. Canada (1923) **17**, III: 125-129, pl. 1.

The rise in temperature due to friction caused a perceptible diminution in the intensity. The intensity also appeared to be proportional to the rate at which the rotating tube was worn away. Friction with steel or other substances softer than quartz produced no tribo-luminescence.

Fluorescence

The name *fluorescence* is generally restricted to radiation emitted by a substance during the passage through it of radiation of a different frequency,—usually a higher frequency.

True fluorescence has been observed only in vitreous silica but not in any of the other modifications or varieties.

Vitreous silica shows a faint green fluorescence under the direct action of X-rays, the light ceasing when the X-rays are cut off. It is succeeded by an actinic phosphorescence, invisible but capable of acting on a photographic plate, and this persists for three or four weeks. It can be destroyed by heating the glass to redness for two minutes.[22]

Becquerel[23] could observe no luminous effect in quartz from concentrated sunlight or the light of an electric spark. Quartz of optical quality shows neither fluorescence nor actinic phosphorescence under X-rays.[22]

A kind of photo-phosphorescence has been observed in electric discharge tubes of vitreous silica. Chapman & Davies[24] observed it when a tube with external electrodes carried a discharge through either oxygen or hydrogen. The glow persisted for 20 minutes or more after the current ceased. Areas cooled with liquid air glowed more brightly than the rest of the tube. The parts where most gas was absorbed glowed the brightest. A greenish phosphorescence was observed by Curtis[25] in a vitreous silica tube containing helium.

Cathodo-luminescence

Certain substances show the phenomenon of *cathodo-luminescence*, that is, if placed opposite the cathode in an electric-discharge tube they glow with light of various colors, the color depending upon the conditions.

Finely divided (micro-aphanitic) silica, produced by volatilization in an arc, and deposited on a metal strip, shows cathodo-luminescence in a marked degree.[26] This luminescence is influenced by the following variables: (1) temperature, (2) pressure of gas in the tube.

The luminescence increases with rising temperature, passes through a maximum, and decreases to zero. The actual temperature limits for silica have not been directly determined, but unpublished observations[27] on a sublimed coating of silica in the cathode tube, in which the bombardment was

[22] Hopwood & Mayneord, Nature (1925) **116**: 98.
[23] Becquerel, E., Ann. Chim. et Phys. (1859) **57**: pp. 46 and 49.
[24] Article cited in note [25].
[25] Curtis, W. E., article cited in note [27].
[26] Nichols, E. L., & Wilber, D. T., Physical Rev. (1921) (2) **17**: 707-717.
[27] Nichols, E. L., correspondence with the author.

carried far enough to heat the central zone to incandescence, indicated that the cathodo-luminescence ceased slightly below the red heat.

The gas pressure has a very marked effect. This effect is presumably exercised through the influence of the gas pressure upon the voltage of the discharge. This relation for the sublimed silica deposit is shown in Figure XXXVIII.1. The effect is reversible with rising and falling gas pressure, and is the same for air, oxygen, and hydrogen.

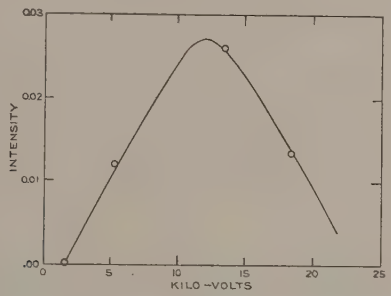


FIG. XXXVIII.1.—Relation of intensity of cathodo-luminescence of sublimed silica to terminal voltage. After Nichols & Wilber, 1921.

The cathodo-luminescence of finely divided silica is affected by temperature similarly to the flame-luminescence (p. 760). It is very likely [27] that the upper cathodo-limit coincides with the upper limit of low-temperature hydrogen-flame excitation, at 367°C.

A kind of cathodo-phosphorescence was observed by Beilby [28] in a lens of quartz which had been exposed for 4 days to the β ray of radium, which is an electron stream. A dark brown spot appeared where the ray entered, which phosphoresced enough to be seen in complete darkness, but ceased to do so within six weeks.

FLAME-LUMINESCENCE

When placed in contact with a burning jet of hydrogen, certain substances, including silica in some of its forms, emit a visible radiation called *flame-luminescence*, which is very different from the radiation due to temperature alone.

This flame-luminescence is greatly influenced by temperature. A certain minimum temperature must be attained before it begins at all. With rising temperature it increases to a maximum intensity and then decreases again, and may finally become zero at an upper limiting temperature. Some oxides show two or more such maxima.

So far as they are now known, these effects can be divided into two classes:

[28] BEILBY, G., *Aggregation and flow of solids* (1921) p. 245.

(1) Low-temperature flame luminescence, occurring at temperatures where no visible radiation is emitted by a black body.

(2) High-temperature luminescence, occurring simultaneously with the visible radiation due to the temperature but sometimes greatly in excess of that radiation. Heating with a flame seems not to be always necessary, although it produces much stronger luminescence than do other means of heating.

Low-temperature flame luminescence

Low-temperature flame luminescence occurs only at the border between hydrogen and oxygen in the flame, toward the hydrogen side of the border. Among the forms and varieties of silica, sublimed silica (from metallic silicon or quartz in an arc) and precipitated silica produce the strongest low-temperature flame-luminescence. Vitreous silica gives none whatever. A crystal of quartz is excited to luminescence only with difficulty.

The low-temperature flame-luminescence from precipitated silica[29] is a pale greenish-white in color. It begins very sharply at 85° and disappears again, with rising temperature, at 367°. It has a spectrum like that which is considered characteristic of true fluorescence, namely, a spectrum consisting of two or more overlapping bands, each band in turn consisting of numerous components which form series having equal frequency intervals.

Not only is there this general similarity, but in certain substances which also show true fluorescence these components of the flame-luminescent spectrum are identical with the components of the true fluorescence excited by light.[30] This comparison can not be made for the luminescence of silica, however, since true fluorescence is rare in the forms of silica, and its spectrum has not been studied.

High-temperature flame-luminescence

When precipitated (micro-amorphous) silica is heated in the oxy-hydrogen flame to temperatures above the red, the first appearance of color in the region of incandescence is not the normal red color but a blue glow. This appears at a temperature so low that the black-body red is still very weak. Add to this the further fact that the intensity is lowered still more by low emissivity, and it is readily understood that the substance when viewed through a red screen, is almost invisible below 800°. It is thus evident that a bluish luminescent radiation peculiar to the substance is being superposed upon the normal radiation due to temperature alone.

This luminescence in silica reaches a maximum at about 1400° and is strong between 1300 and 1500°.

Quantitative data on the high-temperature luminescence of silica have been

[29] Nichols, E. L., & Wilber, D. T., *Flame excitation of luminescence,* Physical Rev. (1921) (2) **17**: 453-468.

[30] Howes, H. L., Physical Rev. (1921) (2) **17**: 469-474.

obtained by Nichols & Howes.[31] The brightness was observed by means of an optical pyrometer with incandescent tungsten filament in the usual evacuated lamp. Direct comparison was made with the brightness of a surface of uranium oxide. Filament and surface were matched in the fairly monochromatic color produced by a red screen (equivalent wave-length 650 mμ) or a blue screen (450 mμ).

The results are given in Table XXXVIII.1. The Table gives the intensity I_o of the light from silica in the two colors stated, in terms of the brightness of the corresponding region of the spectrum of a black body at 1000°. The last two columns give the ratio of this brightness to that (I_{bb}) of a black body at the same temperature. The value 1 therefore indicates that the silica is radiating normally for that temperature and color.

TABLE XXXVIII.1.

HIGH-TEMPERATURE FLAME-LUMINESCENCE OF SILICA. NICHOLS & HOWES, 1922.

Temp. °C	I_o		I_o/I_{bb}	
	Red	Blue	Red	Blue
665	0.000 000 076	0.0382	0.000 59	195
735	0.000 002 6	0.0708	0.002 10	57.3
837	0.000 59	0.341	0.023 9	13.9
960	0.027 5	1.65	0.060 0	3.59
1037	0.191	4.42	0.097 7	2.26
1097	1.10	11.0	0.186	1.86
1190	8.51	35.3	0.316	1.33
1263	41.2	89.1	0.537	1.16
1294	100.0	167	0.865	1.44
1328	233	316	1.31	1.77
1394	614	631	1.58	3.09
1462	1390	1902	1.68	2.30
1527	2500	2566	1.54	1.55

PYRO-LUMINESCENCE

Quartz

The so-called pyro-luminescence of quartz seems to be a case of phosphorescence—revived or delayed phosphorescence.

Pyro-luminescence is a phenomenon exhibited by many specimens of natural quartz. It consists in the production of light when the specimen is heated to a temperature above about 150°C. This natural phosphorescence is not reproducible, lasting only a few seconds or minutes, and not returning on subsequent heating.

The power of pyro-luminescence is restored to the quartz only by exposure to the radiations from radium. Sunlight, the electric spark, the electric arc, and X-rays all are without effect in restoring it.

[31] NICHOLS, E. L., & HOWES, H. L., Physical Rev. (1922) (2) **19**: 300-318. Also Opt. Soc. Amer. etc. (1922) **6**: 42-53.

The most extended study of the pyro-luminescence of quartz is that by Goldschmidt.[32] Quartz specimens from 24 localities were examined, and all but 5 were found to be pyro-luminescent when heated with an alcohol lamp. There was no correlation between this property and either the color or the presence of empyreumatic odor, both of which properties had been supposed by some investigators to be necessarily associated with pyro-luminescence.

About 100 additional experiments were made by Goldschmidt on crystals of quartz from Fefor, Gudbrandsdalen, Norway, to establish the temperature of the luminescence, its duration, and the effects of accompanying conditions.

Pyro-luminescence of artificial origin in quartz was observed by Beilby,[33] when he heated to temperatures of about 100 to 250° a lens which had been exposed to the β ray of radium for 4 days. When the glow had ceased the brown color spot produced by the ray had also vanished.

Pyro-luminescence in vitreous silica

Vitreous silica exposed to ultra-violet radiation undergoes some change which causes it to become temporarily luminescent when subsequently heated. The effect is allied to the photo-phosphorescence already mentioned (p. 756). It has been observed by Baly in using the vitreous-silica-mercury arc lamp. The glass of a 100-volt lamp becomes opaque to the farther ultra-violet after a few days, but its transparency is restored by heating, and pyro-luminescence accompanies the recovery.[34] It has been observed also in electric discharge tubes of silica by Chapman & Davies,[35] Ludlam & West,[36] and Curtis.[37]

Chapman & Davies suspected a relation between absorption of gases (oxygen or hydrogen) and pyro-luminescence, because the effect ceased with the removal of the absorbed gas. It was unaffected by removal of the unabsorbed gas from the tube, and did not lose intensity if the tube had stood undisturbed for a day. Ludlam & West, using hydrogen and the halogens, observed different colors (green and pale violet) from the two parts of a tube made by joining two pieces of tubing, which indicates that some quality of the glass itself has an effect on the luminescence.

Curtis found that the pyro-luminescence in tubes containing hydrogen or helium was related to the distribution of luminosity in the gas during the discharge. This is shown by the very different effects produced by condensed (oscillatory) or uncondensed discharges. After having been destroyed by heating the tube to redness, the luminescent power could be immediately restored by running the tube again, even if only for one second, but the restored luminescence in this case was local and of brief duration. The Lyman series of hydrogen (91 to 122 mμ) was thought to be the radiation responsible for the luminescence.

[32] Goldschmidt, V. M., *Die Pyrolumineszenz des Quarzes*, Forh. Vidensk.-Selsk. Christiania 1906, No. 5: 19 pp.
[33] Place cited in note [28].
[34] Baly, E. C. C., Lecture on *Photo-synthesis* before Chemical Society of Washington, 22 Sept. 1924.
[35] Chapman, D. L., & Davies, L. J., Nature (1924) 113: 309.
[36] Ludlam, E. B., & West, W., Nature (1924) 113: 389.
[37] Curtis, W. E., Nature (1924) 113: 495.

Theories of luminescence

The different kinds of luminescence, including phosphorescence, resemble each other in several important respects, especially in spectral structure, and it therefore seems likely that all will ultimately be brought under a unified theory. At present, investigators are still far from agreement on such a theory.

The characteristic features of the principal theories of luminescence [35] may be crudely compared as follows:

(1) Wiedemann: Reversible molecular changes (general theory).
(2) Lenard: Emission centers, activated by displacement of electrons.
(3) Kowalski: Emission centers of two types, "electronogens" and "lumenophors."
(4) Kennard: Thermodynamic theory; thermal and fluorescent emission independent, and fluorescent energy derived from exciting radiation.
(5) Baly: Absorption and emission related, and occurring only at characteristic frequencies, controlled by opening up of molecular fields, and determined by quantum relations.
(6) Perrin: Photochemical theory; emission when active molecules undergo chemical change produced by exciting agency; frequencies determined by quantum relations.

With the exception of flame-luminescence, quantitative data on the luminescent phenomena of silica are too scanty to permit of much theoretical discussion. Of the theories just mentioned, my personal preference would be for that of Baly, because of its quantitative exactness. Silica might furnish good material for further application of this theory to solids, since we have considerable information on the absorption bands of quartz and vitreous silica (see XXXVI). A relation might be shown between the frequencies of these bands and the spectra of cathodo- and flame-luminescence.

This is on the assumption that silica itself is the active radiating agent. But one of the striking things about luminescence and phosphorescence in general is the part played by minute amounts of a given substance dissolved in another. The solution may be liquid or solid. Either complete removal of the solute or an increase in its concentration may diminish or destroy the luminescence.

We know that nearly all natural quartz contains minute amounts of impurities, usually water, alkalies, alumina, or carbon dioxide. Are these the active agents in the various kinds of luminescence, with silica acting only as a neutral carrier?

If minute quantities of foreign substances are responsible, as is suggested by some of the phenomena, then some high-grade chemical research on the minute impurities in quartz and vitreous silica will be needed

[35] For a fuller review see Merritt, E., *Theories of luminescence*, National Res. Council Bull. 30 (1923) pp. 5-27.

in conjunction with the spectroscopic study. The effect of non-volatile impurities might be traced by converting the quartz or vitreous silica into cristobalite and comparing its luminescence with the original.

Tribo-luminescence

We may suppose that tribo-luminescence arises from the falling into stable positions of certain electrons which, previous to the disruption of the substance, were acting as the combining electrons between the triplets or triplet-chains of silica.

Beals finds the tribo-luminescent spectrum of vitreous silica to be continuous. Would the corresponding spectrum of quartz have a band structure? The inter-atomic distances in the glass may be assumed to have all values within a wide range (p. 261), and the electron-displacements resulting from a fracture cutting across such a heterogeneous set of interconnections might be expected to give a whole series of frequencies. In quartz, on the other hand, the cleavages would be across a limited number of sizes of interconnecting distances, and a band spectrum might result.

Cathodo-luminescence

The cause of cathodo-luminescence is probably a temporary dissociation or ionization of the substance, due to its bombardment by the electron stream. The ions or dissociated parts of the compound then recombine, emitting radiation in doing so.

The effect of voltage upon the luminescence can be explained as follows.[39] Assume that there are two degrees of dissociation; in the one, the parts are separated by so small a distance that they can readily recombine and emit luminescence; in the other, they are separated beyond the possibility of recombination. For each degree of dissociation there is required an electron having an energy greater than a certain minimum, and this necessary minimum is larger for complete dissociation than for temporary dissociation. The number of electrons possessing more than a certain minimum of energy increases with the voltage. Hence with rising voltage the luminescence-producing dissociation will first increase, then decrease as the non-luminescence-producing dissociation begins to gain on it.

Possibly the pyro-luminescence of vitreous silica comes from this non-productive dissociation. If so, its intensity and life ought to be related to the voltage and time of discharge.

Flame-luminescence

Molecular transformations are appealed to by Nichols as the cause of flame-luminescence. The maximum in the curve of silica at about 1400

[39] Nichols & Wilber, article cited in note [26].

is referred to the "well-known transformation of quartz between 1300 and 1500°." The luminescent substance is not quartz, however, but probably cristobalite, since the original material was micro-amorphous (see p. 161); but cristobalite does have an inversion, though a sluggish one, at 1470°, namely the inversion to tridymite. Furthermore, cristobalite has a high-low inversion between 200 and 300°, which may have something to do with the "blue glow" or low-temperature flame luminescence.

We need not suppose that the inversion as we ordinarily see it is actually taking place, forward and back. It may be that the normal effect in silica when a given critical temperature is exceeded is a change of orbit on the part of one of the electrons of the silica atom-triplet, and that the visible inversion is only one of the ultimate results of this orbit-change. What is actually occurring, then, is the rapid to and fro change of orbit of this electron, with luminescent radiation coming off at each return.

In the case of flame-luminescence, the stimulus may come from the radiation emitted when two hydrogen atoms and an oxygen, which have been adsorbed on the silica, combine and evaporate as an H_2O molecule, for heat alone does not produce the luminescence. It would be interesting to compare the luminescent effects of other flames with each other and with the adsorbability of their constituents by silica.

Historical note

The tribo-luminescence of silica was probably the earliest phenomenon of luminescence observed by Man, for he must have noticed it when he first began to make tools and weapons out of chipped flint. Today it remains the least known of the varieties of luminescence. It was repeatedly observed and commented upon by investigators in the 17th and 18th centuries,[40] and there are also scattered observations throughout the 19th century, but no thorough study with modern methods and apparatus. Enough was found out, however, to make it clear that the light is not due to frictional heat or static electric charges.

Pyro-luminescence of quartz has also been known for two centuries or more. The other forms of luminescence in silica are of recent discovery.

[40] For details see KAYSER, H., Handb. Spectroscopie (1908) Vol. 4: 603-627.

Chapter XXXIX. EFFECTS OF STRESS ON THE RADIATIONAL PROPERTIES

In general, any stress has the effect of changing the relative positions of atom-centers and of electron-orbits, and must therefore have an influence on the radiational properties. It is capable of converting an isotropic (unirefringent) substance temporarily into a birefringent uniaxial one, or a birefringent uniaxial substance into a birefringent biaxial.

Stress-birefringence in silica

The effects just mentioned are practically the effects produced in vitreous silica and in low-quartz, the only forms of silica which have been studied in detail.

A piece of isotropic vitreous silica becomes temporarily birefringent when compressed, stretched, or bent. A piece of quartz, under compression or tension in a direction at an angle to the axis, ceases to be uniaxial and becomes temporarily biaxial. If the stress has been applied mechanically, the birefringence or the biaxiality disappears when the stress is removed.

Stress-refractive effects in vitreous silica

Index of refraction

Uniform pressure (hydrostatic) has the effect of increasing the index of refraction of most silicate glasses, and there is no reason to expect that the effect is any different for vitreous silica. The order of magnitude of the change is about 0.001 per kilomegabarye (see Tab. XXII.1 for units) but no actual determinations of its amount have been made on vitreous silica.

Non-uniform pressure (non-hydrostatic stress) is a more complicated matter. Its effect on the dimensions of an isotropic substance requires two elastic constants for their complete statement (see XXIII). Correspondingly, two stress-refractive constants are needed in order to state the effect of stress upon refraction in vitreous silica.

Uni-directional stress gives a piece of glass the optical properties of a uniaxial crystal, and the two constants may therefore take the form of the ordinary and extraordinary refractive indices (n_ϵ and n_ω) of such a crystal (see XXX). Many measurements of these stress-indices have been made on silicate glasses, showing that both rays are retarded by compression; this is almost certainly true of vitreous silica also.

Stress-birefringence

In most glasses the ray vibrating ⊥ to the axis (ordinary ray) is the more retarded of the two originally equal waves, making the birefringence negative (see p. 636); this is known to be true of vitreous silica. The birefringence is expressed quantitatively as the difference between the two refractive indices, $n_\epsilon - n_\omega$. It may also be expressed directly in terms of the relative retardation of one of the two polarized waves with respect to the other. The various measurements on glasses have shown that the retardation is directly proportional to the stress.

An *index of temporary stress-birefringence* may then be defined as the relative retardation, in mμ, of the component vibrating ⊥ to the stress, over the component vibrating || to the stress, when traversing a thickness of 1 cm of a substance submitted to a uniform one-dimensional stress of 1 megabarye; tension being taken as positive.

The index of temporary stress-birefringence for vitreous silica at room temperature is +3.47 for sodium light. This is a little higher than for any of the true silicate glasses so far investigated. These glasses have values for the index ranging from −1.96 to +3.26.

The index of temporary stress-birefringence changes with the frequency of the radiation. In the visible spectrum the change is relatively small for the silicate glasses (a decrease of 3 to 5 per cent from 450 to 650 mμ) and is probably also small for vitreous silica.

The experimental data

The only exact measurement of stress-birefringence in vitreous silica that I am acquainted with is by Heymans & Allis,[1] made by means of bending experiments on a bar of fused silica obtained from the General Electric Co. at Lynn, Massachusetts.

Data on silicate glasses have been published by Adams & Williamson,[2] Pocke's,[3] and Filon.[4,5] Certain borosilicate glasses exceed vitreous silica in stress-birefringence. These are included among the glasses studied by Pockels,[3] Filon,[5] Harris,[6] and Savur.[7]

Harris found that the stress-birefringence of some of his glasses had changed appreciably with the lapse of years. Similar ageing must go on in vitreous silica, and might be examined by repetition of Heymans & Allis' measurements on the same bar after five or ten years, since their specimen was probably fresh.

[1] Heymans, P., & Allis, W. P., Journ. Math. & Phys., Mass. Inst. Technol. (1923) **2**: 216-233.
[2] Adams, L. H., & Williamson, E. D., Journ. Wash. Acad. Sci. (1919) **9**: 609-623.
[3] Pockels, F., Ann. d. Physik (1902) (4) **7**: 745-771.
[4] Filon, L. N. G., Proc. Cambridge Phil. Soc. (1900-1904) **11**: 478-492; **12**: 55-64, 313-337.
[5] Filon, L. N. G., Phil. Trans. Roy. Soc. Lond. (1907) A **207**: 263-306.
[6] Harris, F. C., Proc. Roy. Soc. Lond. (1924) A **106**: 718-723.
[7] Savur, S. R., Phil. Mag. (1925) **50**: 453-463.

Strain and annealing

Reference has been made above only to mechanical stress. Another way of applying stress is by non-uniform heating. If an initially isotropic piece of vitreous silica is heated or cooled unequally, the difference in thermal expansion between the hotter and colder parts produces a stress and a resulting strain in the whole piece. The strain disappears when the temperature again becomes uniform.

The strain found in a cooled piece of vitreous silica, or of any other glass, which has not been completely annealed, has a similar origin. A cooling fragment can never be wholly uniform in temperature, since heat is being radiated and conducted away from the outer surface and flows toward that surface from the interior by virtue of a thermal gradient from the inside outward. This gradient changes as the temperature falls. Hence stresses are set up by the changing amounts of relative expansion.

The piece, if originally fluid, remains unstrained so long as it is capable of flow in response to the stresses set up by the changing gradient. When flow ceases, the changing gradient produces a stress which is permanent, accompanied by a correspondingly permanent strain and birefringence.

If the rate of flow of a glass diminishes continuously with the temperature, as is generally assumed to be the case, it is evident that a completely unstrained piece of glass is an impossibility. On the other hand, a substance which had a definite flow-temperature, above which it was fluid and below which it had no fluidity whatever, could be completely annealed. It would need only to be held at its flow-temperature until the temperature of the piece was uniform throughout. It could then be cooled at any desired rate, since all stresses produced during cooling would be temporary and would disappear when the cooling was complete and the temperature of the piece again became uniform.

This is the fundamental mechanical philosophy of annealing.[8] Its chemical philosophy has been discussed elsewhere (see p. 254).

For practical purposes, most glasses have a flow-temperature of the kind just described, called the "annealing-temperature." With given conditions of cooling, size of piece, etc., the annealing-temperature is so selected that the flow occurring under temporary stress below that temperature is very small. This small flow is ultimately embalmed in the cold glass as a permanent strain, and this strain must be less than the amount permitted by specifications.

Stress-refractive effects in quartz

The effects in quartz are much more difficult to describe than those in vitreous silica. As already stated, the general effect of a stress is to

[8] For a more detailed discussion see Adams, L. H., & Williamson, E. D., J. Franklin Inst. (1920) **190**: 597-631, 835-870.

change quartz from uniaxial to temporary biaxial. For stresses ⊥ to the axis, the plane of the binormals of the temporarily biaxial crystal is ‖ to the direction of stress. The true birefringence ‖ to the axis is proportional to the pressure. The rotatory power remains unchanged, but pure rotation exists now along the two directions of the binormals, instead of along the axis as in unstressed quartz.

The angle between the binormals is 5.96 degrees for a pressure of 100 megabaryes ⊥ to the axis. The angle can be shown to be approximately proportional to the square root of the pressure, for small pressures.

For a complete description of the refractive effect of any stress in quartz we must go back to the equations of elastic deformation.

The index ellipsoid (see XXX) of any crystalline substance is described and oriented in the crystal by means of 6 coefficients (a_{11}, a_{22}, a_{33}, a_{23}, a_{31}, and a_{12}) called the *polarization-constants*. Each of these is changed by stress, and if the stress is not too large the change is expressed by an equation of the type

$$\Delta a_{11} = p_{11}x_x + p_{12}y_y + p_{13}z_z + p_{14}y_z + p_{15}z_x + p_{16}x_y$$

where x_x, etc., represent the 6 components of strain (see XXIII) and p_{11}, etc., are constants known as *elasto-optic constants;* or by

$$\Delta a_{11} = \pi_{11}X_x + \pi_{12}Y_y + \pi_{13}Z_z + \pi_{14}Y_z + \pi_{15}Z_x + \pi_{16}X_y$$

where X_x, etc., represent the 6 components of stress, and π_{11}, etc., are the so-called *piezo-optic constants*. The two sets of constants are of course interdependent.

The general case thus calls for 36 constants such as p_{11} *or* π_{11}, as compared with the 21 constants of elastic theory. Considerations of symmetry reduce this number in the case of low-quartz to 8, as compared with 6 for elasticity (see p. 435). Their values for sodium light, as determined and recalculated by Pockels,[9] are given in Table XXXIX.1. The magnitudes are very similar to those of calcite, the only other uniaxial crystal which has been investigated.

These constants may be expected to vary with the frequency, but the character of the variation is not known.

TABLE XXXIX.1.

STRESS-REFRACTIVE CONSTANTS OF LOW-QUARTZ FOR SODIUM LIGHT.

Unit of stress, 1 kg per sq. mm. (see Table XXII.1).

$p_{11} = +0.138$	$\pi_{11} = +10.9 \times 10^{-6}$
$p_{12} = +0.250$	$\pi_{12} = +24.6 \times 10^{-6}$
$p_{13} = +0.259$	$\pi_{13} = +19.3 \times 10^{-6}$
$p_{14} = -0.029$	$\pi_{14} = -0.95 \times 10^{-6}$
$p_{21} = +0.258$	$\pi_{31} = +27.2 \times 10^{-6}$
$p_{33} = +0.098$	$\pi_{33} = +1.8 \times 10^{-6}$
$p_{44} = -0.0685$	$\pi_{44} = -9.91 \times 10^{-6}$
$p_{41} = -0.042$	$\pi_{41} = -3.14 \times 10^{-6}$

[9] POCKELS, F., *Lehrbuch d. Kristalloptik* (1906) p. 484.

From the signs and magnitudes of the constants it follows that unidirectional pressure || to the axis in quartz decreases its birefringence.

Uniform (hydrostatic) pressure increases the refractive indices, but increases both of them to about the same degree, so that the birefringence is unchanged.

The experimental data on quartz

The most complete quantitative study is that of Pockels.[10] He used six rectangular prisms of the same Brazilian left-quartz as was used by Voigt for the elastic constants (p. 464). Pressures of about 20 to 80 megabaryes were used, and the retardations were measured with a Babinet compensator. The angle between binormals for a given pressure ⊥ to the axis could be calculated from the constants so obtained, and was found to agree with the measured angle.

A very thorough piece of work on the stress-biaxiality of quartz is that of Beaulard.[11] He applied pressures up to 520 megabaryes to the edges of a plate of quartz cut ⊥ to the axis. Polarized light was passed normally through the plate and ⊥ to the direction of pressure, and the vibration-ellipses of the emergent light were examined by means of Senarmont's analyzer. In another series of experiments the pressure was held constant at 191 megabaryes, while the phase-difference of the two waves and the axial ratios of the vibration ellipses were measured for light at various angles to the axis.

All numerical results were found consistent with the assumptions of constant rotatory power at all pressures, and axial birefringence proportional to the pressure. His measurements of axial angles are also in reasonable agreement with Pockels' constants.

Beaulard's calculated effects on the refractive index are, however, considerably in error on account of wrong assumptions concerning the piezo-optic constants.[12]

Constancy of rotatory power had already been shown directly, though less accurately than in the foregoing investigations, by the experiments of Mach & Merten.[13] They examined the interference color patterns of quartz with polarizing apparatus and a didymium glass plate, and showed how the phenomena were explainable only on the basis of constant rotatory power.

Investigations similar to that of Beaulard have been made also by Monnory[14] and by Dongier.[15]

[10] Pockels, F., Ann. d. Physik u. Chem. (Wiedemann) (1889) **37**: 269-305.

[11] Beaulard, F., *Sur la coexistence du pouvoir rotatoire et de la double réfraction dans le quartz.* Thèse, Paris, 1893. 155 pp., 12 pls.

[12] Pockels, F., Lehrb. Kristalloptik (1906) p. 486.

[13] Mach, E., & Merten, J., Sitzungsb. Akad. Wiss. Wien, Math.-Nat. Cl. (1875) **72, II**: 315-328.

[14] Monnory, Compt. rend. Acad. Sci. Paris (1891) **112**: 428-430.

[15] Dongier, R., Ann. Chim. et Physique (1898) **14**: 448-526.

Chapter XL. ELECTRO- AND MAGNETO-RADIATIONAL PROPERTIES

As we have seen in Chapters XXVI to XXIX, both the electric and the magnetic field affect the dimensions and the energy content of silica. The effects must ultimately be explained in terms of the reactions between these fields and the magnetic and electric fields of the electrons which revolve in orbits in every atom of the substance. It is reasonable to expect, therefore, that an electric or a magnetic field will also produce an effect on the transmission of radiant energy through the substance, that is, on the properties which we have been calling "radiational."

General classification

The effects of both the electric and the magnetic field may readily be divided into two groups:

(1) Effects which do not reverse with reversal of the field;
(2) Effects which reverse when the field is reversed.

Non-reversing electrical effects

Certain liquids, placed in an electric field, become birefringent. This electro-birefringence has been thought to occur in silicate glasses, and might therefore be looked for in vitreous silica, but its existence in glasses has been questioned and has not been certainly proved.

Non-reversing effects have not been observed in quartz; it is a substance without a center of symmetry, and opposite directions are not in general equivalent, so that effects reversing with the field are the ones to be expected.

The other forms of silica have not been investigated.

Reversing electric effects in quartz

The effect of an electric field on the refractive properties of quartz is very much the same as that of a mechanical stress; the substance, originally uniaxial, is rendered biaxial (see XXXIX).

This might have been foreseen from the facts described in earlier chapters of this book. Stress produces deformation in quartz (Chapter XXIII) and also causes the separation of electric charges—an electric field (XXVII); conversely, an electric field produces deformation (XXVII); stress also produces biaxiality (XXXIX); hence the electric field must produce biaxiality. But it does not follow that the amount of the biaxiality is also predictable. The electric field may have a refractive effect all its own, in addition to what it produces by way of stress, and experiment shows that it has just such an independent effect.

The effect on the rotatory power, if any, is too small to be taken into account in the measurement of the changes in birefringence.

For a general statement[1] we go back, as before (XXXIX) to the index ellipsoid of the radiation, described and oriented by the six polarization-constants, a_{11}, etc. Each of these is subject to change by the electric field. The change is expressible in terms of the three components of the electric moment per unit volume by means of a linear equation, and the general case therefore requires $3 \times 6 = 18$ *electro-optic constants.*

The symmetry of low-quartz reduces the number of constants to 2. It follows also that the component of the field $\parallel$ to the axis of the quartz is without effect on the refraction, and therefore only the components $\perp$ to the axis need be considered.

If the rotatory power is not influenced by the field, it follows further that the magnitude of the angle of the binormals, and also the birefringence along the axis, are independent of the orientation of the field.

The plane of the binormals, on the other hand, depends on the orientation of the field. When the field is rotated 360° about the axis, the plane rotates 180°.

The constants a, b, and c of the Fresnel ellipsoid are expressed by:

$$a^2 = \frac{1}{n_\omega^2} + e_{11}M \qquad b^2 = \frac{1}{n_\omega^2} - e_{11}M \qquad c^2 = \frac{1}{n_\epsilon^2}$$

where e_{11} is one of the two electro-optic constants, and M is the induced electric moment in the direction of the field, assumed in this case to be $\parallel$ to the X-axis in Figure XXVIII.4.

The other constant, e_{11}, does not enter into the form of the index ellipsoid but only into its orientation, and is therefore a factor in birefringence only at some other angle to the axis than 0 or 90°. The excess path-difference due to a field $\parallel$ to the Y-axis is: $e_{41}M \sin 2\Theta$, where Θ is the angle with the axis.

The constants e_{11} and e_{41} have been expressed above in terms of the induced electric moment M. Their determination in terms of an applied potential accordingly involves a knowledge of the dielectric constant. If this is given the value 4.6 $\perp$ to the axis (XXVI), the electro-optic constants are (in absolute electrostatic units):

$$e_{11} = 4.9 \times 10^{-9} \qquad e_{41} = 2.0 \times 10^{-9}$$

The values which these constants would have, if the biaxiality were due entirely to the stress corresponding to the electric field, are readily calculated from the piezo-electric (XXVIII) and the elasto-optic (XXXIX) constants, and are:

$$e'_{11} = 2.35 \times 10^{9} \qquad e'_{41} = 1.57 \times 10^{-9}$$

[1] For full discussion see POCKELS, F., N. Jahrb. Mineral. etc. (1890) Beil.-Bd. 7: 201-231. Also pp. 85-99 of article cited in note [6].

Since these values are both smaller than the true constants, it is evident that the electric field has a specific influence on the refraction which can not be expressed wholly in terms of piezo-electric deformation.

The differences between the two pairs of constants might conceivably be due to a variation of the dielectric constant with the field intensity. But in this case, the difference $e_{41} - e'_{41}$ should be zero.[2] Since it is quite large enough to be measurable, the explanation will not hold.

The experimental data on electro-optic effects

The first measurements to bring out the regularities in the electro-optic behavior of quartz were by Röntgen[3] and by Kundt.[4] Czermak[5] made similar experiments a few years later, and sought a theoretical explanation for the results, but his explanation was incomplete and in part incorrect.

Röntgen and Kundt had supposed that the effects could all be explained as due to the deformation produced by electrification (XXVIII). Pockels[6] made quantitative measurements of the birefringence in various directions in quartz, clearing up the formal theory of the effects and showing that there is a pure electro-optic effect superposed upon that which is explainable in terms of the deformation.

Magnetic effects

The only magneto-refractive effect upon which data are available is the effect of the magnetic field on the rotatory power.

The electric field seems to be without appreciable influence on the rotatory power of quartz. The magnetic field, on the other hand, affects not only quartz but nearly all other substances as well, whether they possess natural rotatory power or not. The plane of polarization of plane-polarized light passing through the substance undergoes a rotation when the substance is in a magnetic field. This effect is known as "magnetic rotatory polarization" or *magneto-optic rotation.*

It belongs to the class of reversing effects (see p. 771) and differs from the natural rotation (see XXXIII) in depending upon the direction of the radiation relative to the magnetic field, instead of its direction relative to the substance. It is therefore doubled in amount by being reflected back over the same path, while the natural rotation is neutralized by such a reflection.

[2] Pockels, F., Nachr. Kön. Ges. Wiss. Göttingen, Math.-Phys. Cl. 1896: 102-113.

[3] Röntgen, W. C., *Ueber die durch elektrische Kräfte erzeugte Aenderung der Doppelbrechung des Quarzes,* Ber. Oberhess. Ges. Nat.-u. Heilk. (1883) **22**: 49-64, 98-116; Ann. Phys. u. Chem. (Wiedemann) (1883) **18**: 213-228, 534-551; **19**: 319-322.

[4] Kundt, A., *Ueber das optische Verhalten des Quarzes in electrischen Felde,* Ann. Phys. u. Chem. (Wiedemann) (1883) **18**: 228-233.

[5] Czermak, P., Sitzungsb. K. Akad. Wiss. Wien, Math.-Nat. Cl. (1888) **97** II a: 301-324.

[6] Pockels, F., *Ueber den Einfluss des elektrostatischen Feldes auf das optische Verhalten piezoelektrischer Krystalle,* Abh. K. Ges. Wiss. Göttingen, Math.-Phys. Kl. (1894) **39**, 206 pp., especially pp. 83-149.

The magneto-optic rotation is in most cases very much smaller than the natural rotation, being usually measured in minutes of arc rather than degrees.

Quantitative statement of magneto-optic rotation

The rotation is found to be directly proportional to the thickness of the substance traversed and to the magnetization-intensity (see XXIX). The magneto-optic rotatory power of a substance is therefore conveniently expressed in terms of its rotation per unit fall of magnetization-potential. For a weakly magnetic substance of the character of silica the fall of magnetization-potential is proportional to the fall of magnetic potential, which is practically equal to lH, where l is the thickness traversed. The rotation-angle $\omega = \frac{\alpha}{lH}$ is thus a characteristic constant of the substance, usually called the *Verdet constant*, α being given in minutes, l in cm, and H in gilbert-per-cm. It is a constant, of course, only for one substance at a given frequency and a given temperature.

Convention as to sign

The magneto-optic rotation is considered *positive* when the rotation is in the direction taken by the circular electric current which would be necessary to produce the magnetic field. Practically all diamagnetic substances, including silica, show positive rotation.

Magneto-optic rotation of silica

From the available evidence it is impossible to say with certainty which of the two, quartz or vitreous silica, has the greater Verdet constant. The best available values, for sodium light, are:

Quartz	0.017 minute
Vitreous	0.015 minute

The magneto-optic rotation of quartz and vitreous silica is approximately the same as that of water, about one-third that of carbon bisulfide, and about one-seventh that of the densest silicate glasses.

Effect of frequency

The factor causing the greatest variation in the Verdet constant is the frequency. In Table XL.1 are given the only available values of the constant for quartz for a series of frequencies.

The dispersion or rate of change of the constant with frequency is a little greater in vitreous silica than in quartz, but the data are not certain enough to permit the selection of a table of values for vitreous silica.

More definite statements can be made regarding the dispersion of the magnetic rotatory power of quartz, in its relation to the natural

rotation. The two rotations maintain a constant ratio over the range of wave-lengths from 220 to 2140 mμ. This fact is worthy of note, because in most of the substances which have been examined such a proportionality either does not exist or is only approximate, the natural rotation having usually a somewhat higher dispersion than the magneto-optic rotation.

Effect of temperature

The magneto-optic rotation of most substances changes but little with the temperature, and some show a constant rotation. In general, the measurements indicate a *decrease* with rising temperature.

Quartz, and probably vitreous silica, show just the opposite effect, namely, an *increase* of rotation, at a given frequency, with rising temperature. The increase is only about 0.01 per cent per degree.

The experimental data on vitreous silica

Measurements on the magneto-optic rotation of vitreous silica have been made by Stierlin (1907) and by Lowry (1912).

Stierlin[7] used two cylinders of 50 and 72 mm length; they were annealed at 800°, with the effect of practically removing irregular strain-birefringence which they showed when first tested.

Measurements in sodium light at 4 field intensities (maximum about 800 gilbert-per-cm) showed that the rotation was proportional to the field within ½ per cent, thus confirming within this limit the validity of the law upon which the existence of the "Verdet constant" is based.

The means of the final measurements are:

Temperature ° C	Specimen	No. of pairs of readings	$10^2\,\omega$ Minutes
25	II	10	14.53
25	II	10	14.68
25	II	10	14.56
			14.59
102	I	20	14.65

An increase of about 0.5 per cent in the constant for 100° rise of temperature is indicated by the data, but the difference is too small to be accepted as certain.

Lowry[8] measured the magneto-optic rotation produced in vitreous silica disks having a total thickness of exactly[9] 24 mm, at 20° and at 3 visible frequencies. The Verdet constant can not be calculated directly from the data, since the field intensity was not measured, and furthermore was not uniform, which precludes calculation by comparison with the measurements on water

[7] pp. 388-394 of article cited in XVIII, note [15].
[8] Lowry, T. M., p. 296 of article cited in XXXIII, note [4].
[9] Correspondence with the author (1923).

and on quartz in greater thicknesses. One measurement on 24 mm of quartz does, however, make possible a comparison. The data are:

Radiation	Wave-length mμ	Rotation per 24 mm Degrees	
		Vitreous	Quartz
Li flame	670.8	1.19	...
Hg arc	546.1	1.89	1.98
Hg arc	435.9	3.17	...

An attempt to obtain more accurate readings with the help of a rod of vitreous silica 100 mm long was not successful, as the triple field of the polarimeter could not be seen through the rod, which instead "gave a splendid demonstration of Airy's spirals."

The data indicate that the rotation of vitreous silica is *less* than that of quartz. Comparison of Stierlin's measurement with those of Borel [10] on quartz, on the other hand, indicates that the rotation of vitreous silica is *greater* than that of quartz. The discrepancy remains unexplained.

TABLE XL.1.

VERDET CONSTANT OF QUARTZ AT VARIOUS FREQUENCIES. BOREL, 1903.

Source	Wave-length mμ	Verdet constant $10^5\omega$	
		At 20°	At 96°
Cd 25	219.462	158.66	....
Cd 18	257.304	107.90	....
Cd 9	361.25	46.17	....
Cd 6	467.815	27.50	27.72
Cd 5	479.991	25.74	....
Cd 4	508.582	22.57	....
Na (mean)	589.29	16.64	16.82
Cd 1	643.847	13.68	13.79

It is possible that both measurements are correct, and that the magneto-optic rotation of vitreous silica is very susceptible to changes in the internal constitution of the material. The effect of ageing of the glass on its elastic properties (p. 450) and on its stress-birefringence (p. 767) have already been mentioned.

THE EXPERIMENTAL DATA ON QUARTZ

The magneto-optic rotatory power of quartz has been measured for various frequencies by Borel (1903). These are the only absolute measurements of the Verdet constant for quartz. Disch (1903), Lowry (1912), and Ingersoll (1917) have made comparisons with the natural rotation.

[10] See note [11].

Borel [11] used equal thicknesses of dextro- and levo-quartz, each 59.3755 mm, compensating exactly the natural rotation; and measured the magnetic rotation in fields of 1050 to 1420 gilbert-per-cm, with 5 visible and 3 ultra-violet frequencies, at temperatures of 20 and 96°. The sources were a sodium bromide flame and a cadmium spark. Rotation was measured by the methods of Laurent and of Lummer. The results, with recent standard values for the wave-lengths, are given in Table XL.1.

The effect of temperature, between 20 and 100°, is expressed by the formula

$$\omega_t = \omega_{20} [1 + 0.00011 (t - 20)]$$

Lowry [12] measured the magneto-optic rotation of quartz at 6 frequencies in the visible spectrum. He used 4 pieces of dextro-quartz [13] of total length 100.29 mm in series with 4 pieces of levo-quartz [13] of length 98.83 mm, leaving 1.46 mm uncompensated. The temperature was held accurately constant at 20°. The results show nearly perfect constancy in the ratio of magnetic to natural rotation.

Disch [14] measured both natural and magnetic rotation in quartz, using the Lippich triple-field apparatus, and a field of about 3800 gilbert-per-cm calibrated in terms of carbon bisulfide. The sources were a sodium flame (filtered), hydrogen tube, and mercury arc. The ratio of magnetic to natural rotation was found to change progressively by a total amount of about 5 per cent, but the author considered the ratio constant within the limits of error.

The magneto-optic rotation of quartz in the ultra-red has been compared by Ingersoll [15] with its natural rotation, by a differential bolometer method already briefly described (see p. 660). Measurements were made at 23 frequencies from 0.5495 μ (visible) to 2.14 μ, in a field of approximately 9400 gilbert-per-cm.

Ingersoll also made a few tests of the temperature coefficient of the magneto-optic rotation of quartz in the ultra-red, using the interval from room temperature to about 120 to 140°C. Because of the small changes involved, the coefficient proved hard to determine with any accuracy. "The figures obtained, however, indicate a value somewhat higher than for the natural rotation." Details have not been published.

The ratio of magnetic to natural rotation varied irregularly between 0.0123 and 0.0129. In view of the small value of the magneto-optic rotation, this variation is within the limits of error, and the proportionality found by Disch and by Lowry for the visible and ultra-violet is thus confirmed for the ultra-red.

Comparisons

Since the field intensity in each set of measurements is unknown but constant, the best way to compare the results of Disch, Lowry, and Ingersoll

[11] Borel, A., *Sur la polarisation rotatoire mangétique du quartz,* Arch. sci. phys. nat. (1903) **16**: 24-49, 157-171.

[12] Lowry, T. M., pp. 294-295 of article cited in XXXIII, note [4].

[13] See XXXIII, note [5].

[14] Disch, J., *Über Beziehungen zwischen natürlicher und elektromagnetischer Rotationsdispersion,* Inaug.-Diss. Freiburg i.B. 1903, 50 pp., 2 pls.; extract in Ann. Physik (1903) (4) **12**: 1153-1157.

[15] Ingersoll, L. R., article cited in XXXIII, note [27]

with each other and with those of Borel is to use the ratio of each rotation to the rotation at some common frequency as standard. The only frequency common to the four is the D line of sodium. The ratios are given in Table XL.2. Ingersoll's original data have not been published, and his values are therefore taken from his curve (his Table I) but his actual measurements were made at frequencies at or near those listed.

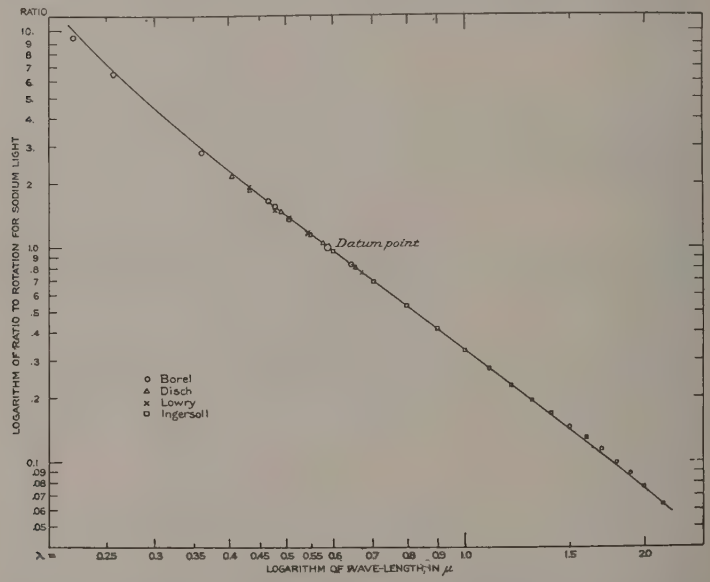


FIG. XL.1.—Diagram to illustrate the relation between dispersion of the magneto-optic rotation and dispersion of the natural rotation of quartz. The points represent the data on magneto-optic rotation, while the curve applies to the natural rotation (Chap. XXXIII).

As a whole, the data show good agreement. The close proportionality between magneto-optic and natural rotation is seen by comparing the plotted points in Figure XL.1, which are the data of Table XL.2, with the curve which is drawn in the same Figure. This curve represents the ratios of *natural* rotations to the rotation at the D line. Although drawn to represent a very different set of data, it is seen to fit the points in Figure XL.1 very closely.

Historical note on magneto-optic rotation

The phenomenon of magneto-optic rotation was first observed by Faraday in 1845, in certain liquids and glasses. In his earlier experiments he could observe no effect in brirefringent crystalline substances, but in 1846 both he

and E. Becquerel[16] found that quartz and some silicates, when placed in a magnetic field, show the property of rotating the plane of polarization. Lüdtge[17] went further and showed that the rotation exists for directions of transmission inclined to the optic axis of quartz. Quantitative measurements on quartz were not made until about fifty years later.

TABLE XL.2.

DISPERSION-RATIOS OF MAGNETO-OPTIC ROTATION OF QUARTZ.

Radiation	Wave-length mμ	Ratio to D line			
		Borel	Disch	Lowry	Ingersoll
Cd 25	219.462	9.534	....	....	....
Cd 18	257.304	6.484	....	....	....
Cd 9	361.25	2.775	....	....	....
Hg	404.656	....	2.137	....	....
Hg	435.834	....	1.852	1.912	....
Cd 6	467.815	1.653	....	....	....
Cd 5	479.991	1.547	....	1.477	....
Hg	491.60	....	1.456	....	....
Cd 4	508.582	1.356	....	1.372	....
Hg	546.072	....	1.171	1.175	....
	549.5	....	....	....	1.158
Hg	579.066	....	1.041	....	....
D	589.29	1.000	1.000	1.000	1.000
	600.	....	....	....	0.963
Cd 1	643.847	0.822	....	....	....
H	656.278	....	0.800	....	....
Li	670.786	....	....	0.760	....
	700.	....	....	....	0.690
	800.	....	....	....	0.529
	900.	....	....	....	0.415
	1000.	....	....	....	0.330
	1100.	....	....	....	0.269
	1200.	....	....	....	0.224
	1300.	....	....	....	0.1915
	1400.	....	....	....	0.1663
	1500.	....	....	....	0.1444
	1600.	....	....	....	0.1266
	1700.	....	....	....	0.1125
	1800	....	....	....	0.0987
	1900.	....	....	....	0.0869
	2000.	....	....	....	0.0761
	2140.	....	....	....	0.0627

EFFECT OF THE MAGNETIC FIELD UPON ABSORPTION

A magnetic field may be expected to influence the absorption of radiation. The effect has been found experimentally only in crystals with narrow absorption bands. Becquerel demonstrated it in the uniaxial crystals xenotime and tysonite. When the optic axis is || to the field the narrow bands are doubled, and correspond to oppositely circularly polarized

[16] BECQUEREL, EDM., Ann. Chim. et Phys. (1846) (3) 17, p. 445.
[17] LÜDTGE, R., Ann. Phys. u. Chem. (Pogg.) (1869) 137: 271-288.

vibrations. The effect evidently depends upon the influence of the field upon the orientation of the electron-orbits producing the absorption. So far as I am aware, it has not been sought for in silica, but some information might possibly be gained on the electron-orbits in silica if a detectable effect could be produced on the silica bands.

Electric and magnetic effects in suspensions

Finely divided substances suspended in a liquid exhibit birefringence and pleochroism in an electric or magnetic field. The effects are probably due to orientation of the particles in the field.

Procopiu[18] has shown that the birefringence, in a magnetic (or electric) field, of a composite liquid consisting of a fine crystalline powder suspended in a liquid of the same average index as the powder, will be *positive* if the optical character and the magnetic (or electric) character of the crystalline substance are alike (both positive or both negative); while it will be *negative* if the optical and magnetic characters are opposite in sign. Thus quartz, which is optically positive but magnetically negative, gives, when in suspension in benzyl alcohol, a liquid which shows negative birefringence in a magnetic field.

So far as I know, the observations on silica have been confined to suspended quartz, but the method might be found useful in the study of the micro-crystalline forms.

[18] Procopiu, S., Compt. rend. Acad. Sci. Paris (1921) **173**: 353-355.

Part 8. Applications

Chapter XLI. GEOLOGICAL APPLICATIONS

The preceding chapter closes the fundamental part of this book, the part that was most difficult to write and that I hope will be of most permanent value; but it has extended to such a length that not much space can be allowed for applications of the facts to various branches of natural science and technology. A few selected examples should be sufficient, however, for if the facts and principles have been successfully presented the reader is better qualified to make applications to his own problems than is the author.

As silica is by far the most abundant and most generally distributed oxide of the Earth's outer shell, its properties enter into many of the problems of cosmology and geology. Chapter II introduces one of these problems, which, though not peculiar to silica, is better elucidated by the data there presented than by any other data now available. This is the problem of the distribution of isotopes.

Silicon isotopes and the Earth's early history

The constancy of isotopous composition of terrestrial and meteoritic silicon was commented upon in Chapter II. The fact has some important consequences. Let us assume that meteorites are fragments of some unknown planet M, an assumption for which there is evidence. Then it follows from the constancy of composition that if silicon isotopes were ever produced in varying proportions in the Solar System, the product was thoroughly mixed before the Earth and planet M were separated out as independent units. Furthermore, the silicon of the Earth's deep interior must have the same composition as the silicon in its present outer shell, for if there had been differentiation of silicon in the Earth, the shell would now differ from M; but it does not.

Looking back over the history of the Earth as we know it from the geological record, we see that the usual course of terrestrial affairs is toward differentiation, not toward uniformity. Constancy in the composition of isotopous elements, though very satisfying to the chemist's peace of mind, is hardly what we might have expected. Whether a particular proportion of isotopes in an element is the result of a definite course of evolution which yielded just that proportion and no other, no matter where it occurred; or whether it is the result of some previous thorough mixing of the material in our part of the Solar System so that it was everywhere the same;—in either case, there would seem to have been abundant opportunity for differentiation during the Earth's subsequent history.

Suppose we start afresh with the assumption that there has in fact been a differentiation of atomic silicon, either alone or in its compounds, accompanying that differentiation of the compounds themselves which we know to have occurred; so that the silicon of the Earth's present granitic shell is something different from the silicon in the deep interior. It follows at once that meteorites are not fragments of a planet *M*, but of the Earth itself. The explosion theory of the Moon's origin immediately comes to mind.[1]

Records in silica minerals

It is part of the task of geology to decipher the past history of the Earth from the present properties of the rocks at and near the Earth's surface. The relative position, the structure, and the composition of the rocks are properties which were easily accessible to the pioneers of the science. Now that the geologist has sketched the broad outlines of Earth history on the basis of these criteria, he has begun to delve further into the available record and to ask questions not only of the rocks as units but of their constituent minerals as well. Probably every mineral in a rock carries some evidence of its past history, which would be an open book to us did we but know what permanent changes of properties are brought about by given conditions of temperature, pressure, and chemical environment.

Silica, because of its variety of forms, its reluctance to change, and its wide distribution, would seem to be one of the best substances from which to decipher the record. It is bound to be increasingly used for this purpose as our knowledge of it progresses. In this section I shall endeavor to show some ways in which it has already been used as an index to the conditions of the past.

If some of the statements seem so obvious as to be hardly worth setting down, the reader may be reminded that it has been only a few years since the plutonists were convinced that basalt is a sedimentary rock, and even fewer since the assumption that a pegmatite is intruded as an igneous dike needed no argument. Some of the things that are most obvious to us are going to be doubted by our successors, so we do well to set them down clearly and prepare to defend them.

Quartz and geological thermometry

The mere presence of quartz in a rock has certain implications. If there is other evidence that the quartz grew where we now find it, we may be certain that the temperature at that point was not above 870°C when the quartz was crystallizing there, provided that the pressure was not far from atmospheric. Even if the pressure was high, the temperature could not

[1] This subject was considered in more detail in one of a series of lectures by the author at the Massachusetts Institute of Technology in April, 1926.

have been much above this value. This is true quite regardless of what or how many other substances were present when the quartz crystallized.

It can not be asserted that such a rock has never been above 870° since it was formed, for quartz will stand heating, even to 1500°, for a short time; but it can be stated positively that the rock has not been above 870° for more than a brief time,—say a few days.

Coming a step lower down on the temperature scale, it is frequently possible to say whether the quartz in a given occurrence has been crystallized above or below the inversion-temperature, 573°. The following facts supply the criteria:[2, 3]

(A) As the temperature diminishes, there is at the inversion-point a sudden decrease in the volume and an increase in the axial ratio of quartz (XX).

(B) High-quartz differs in symmetry from low-quartz and therefore has a different habit of growth (XXV).

(C) Twinning of the Dauphiné type is a common result of the inversion from high-quartz to low (XII).

(A) Evidence of volume-change

Quartz phenocrysts usually break out of a rock easily, compared with feldspar and other minerals. One possible reason for this is that the quartz may have cooled from a temperature above 573°, and in passing through the inversion has broken away from the surrounding minerals because of the sudden change of volume.

Quartz is sometimes found in a cracked and broken state in rocks which do not show any other evidences of pressure or flow. It is possible that such quartz has been broken by stresses set up during its inversion, the enclosing material at that time having been fluid enough to fill the volume left by the sudden shrinkage of the quartz.

Wright & Larsen found that the cracking due to inversion is well brought out by etching with hydrofluoric acid.

(B) Evidence from face development

Strongly marked hexagonal symmetry in natural quartz is presumptive evidence that it formed above 573°. The occurrence of 6 equally developed steep rhombohedrons or of 6 equally developed trapezohedral or parallelogram (pyramidal) faces is nearly certain evidence. The occurrence of 6 equally developed primary rhombohedrons (the common forms $\{10\bar{1}1\}$ and $\{01\bar{1}1\}$) is less certain, because low-quartz is known to grow in this habit.

Marked trigonal symmetry is nearly certain evidence of formation below 573°.

[2] Mügge, O., Neues Jahrb. Min. (1907) Festbd., pp. 181-196.

[3] Wright, F. E., & Larsen, E. S., Amer. J. Sci. (1909) **27**: 421-447; Zeitschr. anorg. Chem. (1910) **68**: 338-369.

(C) Evidence from Dauphiné twinning

Dauphiné twinning in natural quartz, taken by itself, does not have decisive weight as evidence of the temperature of formation. It may have resulted from the inversion, or it may have resulted from growth at low temperatures.

The character of the composition-surface between two units of the twin has been proposed as a criterion, Wright & Larsen [4] holding that a curving and irregular surface is evidence that the twinning was due to inversion and therefore that the quartz showing such surfaces was formed above 573°. But Mügge [5] has found that similarly irregular and curving boundaries exist in quartz which the combined evidence of face development and twinning shows certainly to have been formed below 573°.

The entire absence of Dauphiné twinning is presumptive evidence of formation below 573°, but not certain proof, since it is possible to cool high-quartz through the inversion without the production of any twinning.

In judging whether Dauphiné twinning is or is not present, attention must be paid to cracks in the quartz. The crystal often breaks along a twinning boundary; hence the section as a whole must be considered and not merely a portion bounded by cracks.

Combined evidence from Dauphiné twinning and face development

Dauphiné twinning in many occurrences is expressed in external form, as in the interpenetration twin shown in Figure XII.11, or in the fact that the boundaries between twinned units are everywhere consistent with the faces and never cut across a characteristic face such as *x* or *s* (see Fig. XII.7). Such a combination of twinning and face development is certain evidence that the growth of the quartz was *completed* below 573°, and presumptive evidence that the crystal was formed entirely below that temperature. It might, however, have started above 573°, for the twinning caused by an inversion could be expressed in external form through further growth below the inversion-temperature.

Dauphiné twinning in quartz which on other grounds is supposed to have crystallized below 573° is, in the opinion of Mügge, presumptive evidence of an "approximation to the conditions of equilibrium stable above 570°". For pure quartz this can only mean a temperature approaching the inversion-point. This deduction is made by analogy with other mimetic polymorphous substances.

[4] Article cited. The authors apply this criterion also to intergrowths of right- and left-quartz, if present in the specimen.

[5] Mügge, O., *Quarz als geologisches Thermometer und die Bedeutung der Zusammensetzungsflächen von Kristallzwillingen,* Nachr. K. Ges. Wiss. Göttingen, Math. phys. Kl. 1921: 217-222.

Etching

Le Chatelier[6] has stated that the existence of similar natural etch figures on both rhombohedrons of a quartz crystal is evidence that the etching, and presumably the formation of the crystal, took place above 573°. This conclusion is based upon Friedel's experiments (p. 512). Mügge has shown, however, that this symmetrical etching can be produced below 573°. Hence while sixfold symmetry is a necessary quality of etching done above 573° it is not a sufficient proof of such a temperature.

Below are given a few instances in which the temperature of formation of quartz has been deduced from some of the criteria discussed in the foregoing pages.

Quartz formed above 573°:

Occurrence and locality	Criteria	Author
In spherulitic liparite, Glade Creek, Wyoming.	Hexagonal habit; Dauphiné twinning crossing faces.	Iddings & Penfield (1891), Mügge (1922).
In biotite granite, Lake Bennett, British Columbia.	Fracturing; irregular twinning, areas small.	Wright & Larsen (1909).

Quartz formed below 573°:

Occurrence and locality	Criteria	Author
Hollersbachtal, Ob. Pinzgau.	Agreement of faces with Dauphiné twinning; entire absence of twinning in some specimens.	Mügge (1922).
Schemnitz.	Trigonal habit; agreement of faces with Dauphiné twinning.	Mügge (1922).
Crystal Mt., Hot Springs, Arkansas.	Clear, only few cracks; regular intergrowths; twinning usually regular.	Wright & Larsen (1909).
Intergrowth with graphite, contact zone of pegmatite, Ticonderoga, New York.	Freedom from cracks; regular twinning; regular intergrowths.	Bastin (1910).*

* Econ. Geol. (1910) **5**: 134-157.

Historical note

In presenting his report in 1855 recommending the publication of Des Cloizeaux's monograph on quartz, Senarmont laid special stress on the considerable advance made by Des Cloizeaux in our knowledge of the habit of that mineral, and the correlations that he and others had noticed between habit and geologic associations. He ventured the hope that it would not be

[6] *Silice et silicates* (1914, Paris) p. 121.

long until the relation of habit to conditions of growth would be much more fully understood.

After the lapse of seventy years we are still not much nearer the goal set by Senarmont. Other matters have occupied the attention of physicists, chemists, and mineralogists, and the habit of quartz as related to its conditions of growth has remained only a subject of chance observation, not of planned research.

Des Cloizeaux laid an excellent foundation which should, in the logical order of development, have been followed by experiments on the artificial production of quartz, correlating its resulting habit with the temperature and composition of the solutions or melts. Few such experiments have been made, however. On the contrary, what evidence there is has come from quite the opposite direction: the mineralogists and petrologists have observed the habit of quartz under conditions which they could infer with fair certainty—conditions not very different from those easily accessible to every-day observation in the field. Chemistry and physics have become to that extent dependent upon geology for data, a very unusual state of affairs.

Tridymite and cristobalite

It might appear at first thought that the occurrence of one of the high-temperature forms of silica in a rock is evidence that the rock was above 1470° (cristobalite) or above 870° (tridymite). But the tendency shown by silica to deposit in metastable forms spoils this part of the argument. Cristobalite and tridymite can be deposited at temperatures far below 1470 or 870° (see IV and V).

The occurrence of cristobalite does set an upper limit of 1710°, but no one now suspects any intrusive or extrusive rock of having attained such a temperature. Further, cristobalite usually occurs on the walls of cavities in eruptive rocks which would be fluid, and would therefore have no cavities with permanent walls, if heated to 1470°, and we must therefore conclude that in all such occurrences it has formed as a metastable modification.

On the other hand, a fairly definite lower limit can be set. Both the octahedral habit and the presence of numerous microscopic cracks due to the high-low inversion indicate that natural cristobalite showing these characteristics has been formed above the inversion point, that is, not lower than 220° and possibly higher than 280°C.

Tridymite represents a similar case. Its presence means a temperature certainly less than 1685°, and almost certainly less than 1470°, but these temperatures, again, are higher than those usually assigned to igneous rocks. As with cristobalite, the presence of tridymite on the walls of cavities points to deposition below the temperature of fluidity of the rock, but this temperature will still be within the stability-range of tridymite if above 870°. If there is original intergrowth with quartz, however, the temperature must have been below 870°.

The lower limit is set, as with cristobalite, by the universally present evidences of inversion from one of the high-modifications, but the limit is low,—only 116°,—and therefore not of much use.

Micro-crystalline silica

It has long been assumed that chalcedonic silica and its allied micro-forms are produced at atmospheric temperatures or not far above. Flint was early found by Ehrenberg to contain infusoria, and chalcedony forms part of the replacing silica of a great variety of silicified fossils, including petrified wood. Such associations show that the temperature of deposition of these materials could not have been high.

The opinion is sometimes expressed that chalcedonic silica represents conditions of rapid deposition. This hypothesis seems to rest almost entirely upon *a priori* reasoning and analogy.

The opinion has also been expressed [7] that the formation of chalcedonic silica occurs from supersaturated solutions, the supersaturation having been brought about by rapid cooling. This conclusion appears to be a natural corollary to the foregoing hypothesis that chalcedonic silica is produced by rapid deposition. So far as I know, there is no convincing experimental evidence either for or against these hypotheses of supersaturation and rapid deposition.

The presence of chalcedonic silica thus means very little so far as thermometry is concerned, except to make it probable that the temperature was not above 870°, the upper limit for quartz, which chalcedonic silica so closely resembles. Its interpretation in terms of chemical environment still awaits the necessary evidence from laboratory experiment.

Speculations on piezo-electric and elastic properties

New facts about the Earth-forming minerals are an outstanding invitation to speculate on the causes of geological phenomena. As a contrast to the fairly well-grounded applications made in the pages just preceding, I may perhaps be permitted to offer two suggestions which must not be taken too seriously until tested by quantitative comparisons.

Piezo-electricity

Every change in the stress on a quartz crystal causes a separation of electric charges (XXVIII). The most widespread and persistently active stress-change in the Earth is the semi-diurnal change due to the Moon, expressed in the oceanic and the bodily tides. If the quartz crystals which make up so large a proportion of the outer shell are oriented at random in all possible directions, no external effect might be perceptible, even though the total shifting of electrons is very large in the aggregate. But a perfectly random distribution is the last thing to be expected of crystals growing under the world-wide influence of gravity, the regional influence of large-scale movements in the crust, and such local influences as intrusion. The orientation of crystals in pegmatites and schists is familiar to all petrologists.

[7] For example, by Endell & Rieke, article cited in IV, note [18].

Are there any semi-diurnal or other periodic effects in the Earth's electric field, or even in its magnetic field, which could be referred to piezo-electricity? Until recently, periodicities in the electric field were almost undetectable because of the large local fluctuations at any land station. But through measurements at sea, Mauchly, of the Department of Terrestial Magnetism of the Carnegie Institution, has recently succeeded in finding a periodicity which shows this striking difference from most such periodicities: it is determined by *absolute* time, not by the local time of the station. It must therefore have an interpretation in terms of the Earth's structure, and in that as yet unknown interpretation the piezo-electric effect may have a part. It can not be the leading part, however, for the periodicity is in *solar* time, not lunar.

The principal periodicity in the Earth's magnetic field is likewise solar. But there is, in addition, a small lunar component. Has it a piezo-electric origin?

Elastic properties at the inversion point

The sudden volume-change in quartz at 573° must have important effects on the deformation of rocks which are deep enough in the outer shell to be near that temperature. These effects are obvious enough to need no comment, but attention should be called to the remarkable changes in elastic properties which accompany the inversion (see Fig. XXIII.8). Imagine a deeply buried quartzite whose temperature is rising as a result of conduction from below or of the accumulation of radioactive heat. As the inversion point is approached the axial and equatorial moduli decrease rapidly, which makes it likely that the compressibility undergoes a correspondingly rapid increase. It is even possible that the volume would diminish with rising temperature. At the inversion point there is a sudden increase of volume, which is considerably accentuated by a sudden increase in the moduli or fall in the compressibility. Has this series of phenomena any connection with the well-known geological cycle of a sinking sea-bottom, accumulating sediments steadily until a sudden reversal of the movement lifts the sediments into a mountain-range or plateau? Such a series would be consistent with the facts of isostasy. On the other hand, impossibly great thicknesses of quartzite would be required for the larger vertical movements, unless it be found that the changes in elasticity are of much greater magnitude under pressures of a few thousand megabaryes than they are at atmospheric pressure.

Chapter XLII. SILICA MINERALS AND ROCKS

Modes of natural occurrence of silica

Silica occurs in nature in all of the polymorphous forms described in Chapter IV; in fact, these were all first known as natural minerals before they were made artificially. Most of the micro-forms described in Chapter X also occur as natural minerals. Hydrated silica has not been considered in the main part of this book, but the hydrated minerals must be given at least general mention since they grade over imperceptibly into anhydrous forms.

The general list of natural forms and varieties is then:

Principal phases	Quartz Tridymite Cristobalite Vitreous silica
Micro-forms	Chalcedonic silica (in part) Micro-amorphous silica
Hydrated varieties	Opaline silica Chalcedonic silica (in part)

All of the foregoing are assumed to be pure silica alone or pure silica with water. If we include silica minerals containing small amounts of impurities and coloring matters we have in addition to the above-mentioned pure forms a great variety of *impure silica minerals,* ranging from amethyst to black chert. These will be briefly discussed in a later section of this chapter.

Quartz is the most common and also the most abundant form of silica in nature. By "common" I mean found in a great many places, and by "abundant", found in large quantities. Tridymite is also fairly common, but not abundant. Cristobalite is comparatively rare, though much more common than was supposed a few years ago. Natural vitreous silica is extremely rare.

Chalcedony and chalcedonic silica (flint, etc.), again, are common and fairly abundant, although not so abundant as quartz. Micro-amorphous silica and hydrated amorphous silica are less common, but quite abundant in certain localities.

Quartz

Quartz is a well-nigh universal constituent mineral of the salic [1] igneous rocks (granite, syenite, rhyolite, etc.). It is much less common in the

[1] The salic rocks (term derived from the symbols Si and Al) are those containing 50 or more formula-per-cent of ($SiO_2 + Al_2O_3$). Rocks containing less than this proportion are known as "femic" (term derived from the symbols Fe and Mg).

femic rocks (diorite, basalt, etc.) but is found there not infrequently. It is present in nearly all metamorphic rocks, whatever their origin. It makes up the greater part of the sandstones, and occurs in nearly all shales and clays. Quartzite is a sandstone made up chiefly of quartz grains, which are cemented together by quartz or chalcedonic silica. Quartz is abundant as a vein-forming mineral in association with all kinds of rocks.

Classifications of natural quartz

Probably no minerals appear so often in the dictionary as do quartz and chalcedony, under all kinds of names. This is the natural result of three facts: (1) the abundance of silica, (2) the number of forms and varieties in which pure silica occurs, and (3) the numerous and different-appearing variations produced by small amounts of impurities. Most of these names are based either upon color or upon some feature of external appearance.

Classification by general external form.—The first natural basis of classification is by general external form or manner of occurrence. This gives the following groupings:

Anhedral quartz
Euhedral quartz or *rock crystal*
Pseudomorphous quartz (see p. 797)

Euhedral quartz has received various names depending upon external form. Some of these are listed in Table XLII.1.

TABLE XLII.1.

VARIETIES OF EUHEDRAL QUARTZ, DISTINGUISHED BY EXTERNAL FORM.

Principal characteristics	English name	French name	German name
Well-formed crystals	Rock crystal	Cristal de roche Quartz hyalin	Bergkrystall
Cavities parallel to faces.....	Cavernous quartz		
Separable layers or caps, with clay or other partings.....	Cap-quartz	Quartz encapuchonné	Kappenquarz
Crust of small crystals.....	Drusy quartz		
Separable into radiating parts.	Radiated quartz		
Visible fibers	Fibrous quartz		Faserquarz Faserkiesel

Colored varieties of quartz.—Usually the most striking feature of a mineral is its color. Since pure and homogenous quartz is colorless, having no selective absorption in the visible portion of the spectrum, colored quartz must either contain dissolved or submicroscopic impurities, or be in some manner inhomogeneous.

Table XLII.2 contains the names given to well-crystallized, transparent or nearly transparent quartz of various colors.

TABLE XLII.2.

COLORED, APPARENTLY HOMOGENEOUS, VARIETIES OF QUARTZ.

Color	English name	French name	German name
Clear purple Bluish violet	Amethyst	Améthyste	Amethyst
Indigo Berlin blue	Sapphire-quartz*	Quartz saphirine	Sapphirquarz
Pale blue	Blue-quartz	Quartz bleu	Blauquarz
Yellow	False topaz Citrine	Fausse topaze Citrin	Citrin
Deep yellow Blood red	Ferruginous quartz	Quartz hématoide	Eisenkiesel
Rose red Pink	Rose-quartz	Quartz rose	Rosenquarz
Smoky yellow to Dark smoky brown	Smoky quartz Cairngorm stone	Quartz enfumé	Rauchquarz
Dark brown, nearly black	Morion	Morion	Morion

* Sometimes called "siderite," but this name is now reserved for the mineral ferrous carbonate.

Many specimens of amethyst are intimately twinned, but this twinning is not a necessary accompaniment of the purple color. Conversely, color does not always accompany this variety of twinning. At first, however, the two were so often found associated that twinning was accepted as one of the qualities of all amethyst.

This distinction between amethyst and quartz was worked out in careful detail by Brewster, and was discovered independently about the same time by Herschel while he was studying the correlation of optical rotatory power and face development (see p. 191).

Inclusion-bearing varieties.—Passing now from the homogeneously colored varieties, in which distinct inclusions cannot be seen under the microscope, to varieties in which the size, shape, and even the composition of the impurities can be identified, we get another classification, based upon the size, shape, and composition of the inclusions. Varieties of this class are listed in Table XLII.3.

TRIDYMITE

Tridymite is usually found in *volcanic* rocks, that is, rocks which have been poured out in a molten condition at or near the Earth's surface. Furthermore, it is usually found in the more salic of these volcanic rocks, such as rhyolite, trachyte, and andesite. It has never been found in a sedimentary or metamorphic rock.

Tridymite is a much commoner mineral than petrologists have heretofore supposed. Larsen[2] has found it in a wide variety of effusive igneous rocks, and in amounts up to 17 per cent of the total, a proportion

[2] LARSEN, E. S., personal communication.

which ranks it with the essential constituents of such a rock. Tridymite has undoubtedly been overlooked in some of the earlier descriptions of rocks, perhaps having been erroneously reported as "glass", that is, silicate glass such as occurs in obsidian, not pure vitreous silica.

The supposedly new mineral *asmanite*, described by Maskelyne in 1871, was shown by Winkler & Weissbach[3] to have many of the properties of tridymite, but Sokolov[4] does not consider the identity sufficiently proved.

Granuline is another mineral which may be identical with tridymite, but deserves further examination.

Cristobalite

Cristobalite has been found only in certain volcanic rocks, and only rarely in those. It has never been found in a sedimentary or metamorphic rock.

Vitreous silica

Vitreous silica, usually somewhat impure, has been found at many localities in the form of small fragments, thin sheets of glaze, or small hollow tubes of about 1 cm diameter. The generally accepted explanation of such occurrences is that they are the result of the very high temperature produced by a lightning flash. The tubes are therefore known as *fulgurites* (Latin *fulgur*, lightning).

Fulgurites and fulgurite fragments consist usually of fused silica with a smooth glassy inside surface, and a rough outside surface with adhering grains of sand.

Endell[5] could find no certain evidence of either tridymite or cristobalite in the fulgurite fragments which he found near Schandau, Germany. The glass is evidently the product of the direct and very rapid fusion of quartz, followed by sudden chilling. The 573° inversion of the embedded or adherent quartz grains has had the effect of producing fine cracks in the glass, making the specimens fragile.

Natural micro-fibrous silica

A classification of micro-fibrous-crystalline silica was attempted in Chapter X, on the basis of optical properties, but so few specimens have been examined by the methods used in differentiating those types that it is not practicable to make any general statements regarding their mode of occurrence. It will be necessary to lump them together as "chalcedonic silica".

Chalcedonic silica occurs in salic volcanic rocks; in the deposits of hot springs; in mineral veins; and as concretions or as nodules in sedimentary rocks, especially limestone.

[3] Verh. (Nova Acta) Kais. Leop. Carol. Akad. (1878) **40**: 331-382.
[4] Article cited in XXXII, note [3].
[5] Endell, K., Sprechsaal (1913) **46**: 319-320.

TABLE XLII.3.

INCLUSION-BEARING VARIETIES OF QUARTZ.

Form of inclusion	Character of inclusion	Color in mass	Color of inclusions	English name	French name	German name
Microscopic bubbles.	Air Oils	Milk-white Bluish-white	Colorless	Milky quartz	Quartz laiteux Quartz en chemise	Milchquarz
Grains	Ferric oxide	Red	Red	Ferruginous quartz	Quartz hématoide	Eisenkiesel
	Ferric oxide hydrated	Yellow	Red		Quartz ferrugineux	
Acicular crystals	Rutile (TiO_2)	.....	Red	Sagenitic quartz*	Cheveux de Venus	
	Tourmaline	.....	Black			
Fibers	.....	.....	Brown	Cat's-eye Tiger-eye	Oeil de chat Oeil de tigre	Katzenauge Tigerauge
Streaks	.....	.....	Whitish or various colors	Asteriated quartz Star-quartz		Sternquarz
Scales	Hematite	.....	Red	Aventurine quartz	Aventurine	Avanturinquarz
Scales	Mica	.....	Colorless			
Scales	Chlorite	Green	Green	Chloritic quartz	Quartz chloriteux	

* Especially if needles are in a reticulated (net-like) pattern.

Pure chalcedonic silica is one end-member in a series of natural minerals of the composition ($SiO_2 + H_2O$). The other end-member is *opal*.

TABLE XLII.4.

VARIETIES OF NATURAL MICRO-FIBROUS SILICA.

Color	Other characteristics	English name	French name	German name
TRANSLUCENT, COLOR APPARENTLY HOMOGENEOUS.				
(All types)	Waxy luster	Chalcedony	Calcédoine	Chalcedon
Green	Contains Ni	Chrysoprase	Chrysoprase	Chrysopras
Leek-green		Prase	Prase	Prasem
Bright green	Chlorite inclusions	Plasma*	Plasma	Plasma
Green	Contains red or yellow spots	Heliotrope*	Héliotrope	Heliotrop
Red, Yellowish red	.....	Carnelian	Cornaline	Carneol
Brown	.....	Sard	Sardoine	Sarder
	Contains cavities partly filled with water	Enhydros	Enhydres	Enhydros
BANDED.				
(All types)	.....	Agate	Agate	Achat
White and brown or gray	Banded in planes	Onyx	Onyx	Onyx
White and reddish brown	Banded in planes	Sardonyx	Sardonyx	Sardonyx
OPAQUE.				
Gray to black	.....	Flint	Silex Pierre à feu	Feuerstein
Gray to black	.....	Chert, Nodular chert, Hornstone	Silex de la craie	Hornstein
Red, yellow, brown, green, bluish gray	.....	Jasper	Jaspe	Jaspis

* Some specimens of these green varieties should be classed with the opaque rather than the translucent group.

The essential quality of chalcedonic silica is that its units be of microscopic or submicroscopic dimensions in at least two directions; that is, it is micro-fibrous in structure. It need not be all crystalline, although most of it is quite evidently in that state. Opal, on the other hand, is an amorphous transparent hard gel of silica containing water, the percentage of which may vary from zero to about 12 per cent.

Natural micro-fibrous silica minerals may therefore be looked upon as made up of three constituents: micro-fibrous crystalline silica, amorphous silica, and water.

Following the same lines of differentiation as with quartz, we may next distinguish *impure varieties* of natural micro-fibrous silica, but must depart, for obvious reasons, from the plan used with quartz of distinguishing sharply between homogeneous color and color due to visible inclusions. Table XLII.4 assembles the names and characteristics of the principal varieties of micro-fibrous silica.

The character of the fracture may help in distinguishing the natural varieties. If the fibers are long and are arranged over a distance of some mm or cm in a regular manner,—as parallel or radially,—the fracture will be fibrous. But if the fibers are very short and arranged heterogeneously, the fracture is likely to be conchoidal. Chalcedony will usually show a fibrous fracture; flint and chert, a conchoidal fracture. A distinction sometimes made is that the fracture of chert is more splintery than that of flint.

An example of a chemical method of attack on the problem of differentiation of the varieties is Mellor & Campbell's comparison[6] between the properties of gray and black flint. They found no essential difference in chemical composition, in the proportion of "colloidal" (non-crystalline) silica, or in the total change of density when calcined. They did find, however, a definite difference in the amount of shattering during calcination, for the gray flint shatters more than the black. This was ascribed to a difference in their rates of transformation to cristobalite, since 35 per cent of gray flint is converted at about 1190° as compared with 30 per cent of black flint.

Micro-amorphous and hydrated silica

As noted in the paragraphs just preceding, micro-amorphous silica, usually partly hydrated, is present in most specimens of chalcedonic silica, but the crystalline fibers are the predominating constituent. Varieties in which the micro-amorphous makes up a large part or all of the specimen are not usually called chalcedonic.

Amorphous silica in more massive form, usually hydrated and containing up to about 12 per cent of water, is called *opaline silica*. This group includes the numerous varieties of opal.

Table XLII.5 contains the principal names coming under this general classification.

Opaline silica occurs in cavities and cracks of volcanic rocks; in the deposits made by hot springs; and in some sedimentary rocks, principally limestones and shales, though less commonly than chalcedonic silica. Micro-amorphous hydrated silica occurs in the same associations as opaline silica, and also in extensive sedimentary beds of diatomite (see below).

One of the most interesting of the forms assumed by micro-amorphous and opaline silica in nature is the material known as "diatomaceous earth" or *diatomite*. The minute objects of which true diatomaceous earth is composed

[6] Article cited in V, note [17].

have always been very popular with microscopists, because they are the smallest regularly-patterned objects known to us, and therefore make capital material on which to try the skill of the observer or the capacity of his instrument.

TABLE XLII.5.

VARIETIES OF AMORPHOUS AND MICRO-AMORPHOUS SILICA, MOSTLY HYDRATED.

Principal characteristics	English name	French name	German name
TRANSPARENT OR TRANSLUCENT.			
Colorless, transparent	Hyalite	Hyalite	Hyalit
Iridescent colors	Gem opal	Opale précieuse	Edler Opal
Red and yellow colors, with fire-like reflections	Fire opal	Opale de feu	Feueropal
MICRO-AMORPHOUS.			
White, gray, or brown incrustations of no special external form	Siliceous sinter		Kieselsinter Kieseltuff
Fibrous or filamentous incrustations	Fiorite Pearl-sinter	Fiorite	Fiorit Perlsinter
Concretionary incrustations	Geyserite	Geysirite Geyserite	Geysirit Geyserit Geiserit
Shells or skeletons of microorganisms	Diatomite Diatomaceous earth Infusorial earth Fossil flour Tripoli * Tripolite	Randannite Terres d'infusoires Tellurine Farine fossile Tripoli	Kieselguhr Diatomeenerde Infusorienerde Bergmehl Kieselmehl Tripel

* In the United States the term "tripoli" is used at the present time in the meaning "finely divided micro-crystalline silica." (WEIGEL, p. 10 of bulletin cited in XLIII, note [3].

Each grain is the shell or skeleton of a water-inhabiting organism, and consists of nearly pure hydrated amorphous silica. The living organism itself is but a bit of protoplasm, mostly water, almost completely surrounded by its silica skeleton. When the organism dies its water simply evaporates or diffuses away, leaving a hollow cylinder or ellipsoid. Many of these appear to be completely closed hollow shells, into which nothing larger than a large molecule can penetrate.

Their size is usually of the order of magnitude of 0.01 mm or 10 μ, while the spines, pits, and other symmetrical markings and features which distinguish one species or variety from another grade from 1 μ down to the limit of resolving power of the microscope, 0.5 μ or less, depending on the wave-length

of the light and the relative index of refraction of the surrounding medium. The extreme range of size of the organisms is from about 1 mm down to perhaps 1 μ. The cause of their symmetrical form is a complete mystery. One gets the impression from looking through the illustrations that digonal, trigonal, and hexagonal forms make up the greater proportion, while quadragonal and pentagonal forms are less numerous. This recalls Chapters III, XII, and XV, but how can the symmetry of a molecule affect the symmetry of an amorphous structure? On the other hand, it may be that the impression is false. I am not acquainted with any statistical study of the symmetries of these species, but such a study should yield a fairly definite result, for the species number more than a thousand.

Another type of amorphous silica of organic origin is secreted by sponges in the form known as *sponge spicules*. Radiolaria also secrete opaline silica.

Pseudomorphs and paramorphs

Mineralogists have often observed, but never satisfactorily explained, the phenomenon of the replacement of one crystal by another crystal (or crystalline aggregate) which has a different chemical composition, but which completely preserves the original external form of the first crystal, even to minute details of markings. The second crystal or aggregate is called a *pseudomorph*.

Silica often forms pseudomorphs after other minerals, such as calcite and fluorite, usually replacing them with quartz, and sometimes with chalcedonic silica. The discussion of this subject would open some of the problems of *silicification*, too little understood to be introduced here.

Besides replacing other minerals, silica itself may be replaced, but such pseudomorphs are less common than the obverse type.

Silica exhibits the type of pseudomorphism known as *paramorphism*, in which the pseudomorph has the same chemical composition as the original crystal, but consists of a different modification or variety. Among the four types: quartz, tridymite, cristobalite, and micro-crystalline, 12 such permutations are possible, of which two will be illustrated by examples.

Quartz after tridymite

The best example of paramorphism in silica is *quartz after tridymite*. The original geometric forms and twinning of the tridymite are perfectly preserved, but the material is crystalline quartz. The quartz shows a tendency to be oriented in such a way that the rhombohedrons $\{10\bar{1}1\}$ and $\{01\bar{1}1\}$ of the quartz crystal are parallel to the base $\{001\}$ of the tridymite.

This case of paramorphism was first demonstrated by Mallard.[7] Both Schuster and Lasaulx had already observed that certain supposed tridymite crystals from the Euganean Hills (Colli Euganei) in northeastern Italy,—the best and largest "tridymite" then on record,—had divergent and unexplainable optical properties as compared with the original tridymite of vom Rath. Mallard showed that the material had the birefringence and mean index of

[7] Article cited in IV, note [18].

refraction of quartz, and that it approached quartz in density. Heated to bright red the crystals became opaque and white (inversion to cristobalite) while true tridymite remained unchanged.

Cristobalite after tridymite (?)

An unusual occurrence of cristobalite is described by Ramdohr.[8] It occurs as milk-white crystals less than 1 mm in diameter, in the basalt of the Blaue Kuppe near Eschwege, Germany. There are three varieties: The first consists of octahedrons with occasional cube faces. These grade over gradually by distortion into the second variety, thin six-sided plates bounded by rhombohedral faces, two octahedral faces becoming the basal planes of the plate; spinel twinning is abundant. These again grade into the third variety, hexagonal plates bounded by the hexagonal prism. The twinning is like that of high-tridymite, after $\{10\bar{1}6\}$ and $\{30\bar{3}4\}$. The crystals were assumed to be paramorphs of cristobalite after tridymite but are more probably original cristobalite growing in a habit which imitates tridymite (see also p. 55).

Mutual association of varieties of silica

Two or more forms or varieties of silica may grow side by side, or be intimately intergrown, as if they had formed simultaneously. The commonest association of this kind is quartz and chalcedonic silica.

An interesting feature of some of these intergrowths is the orientin action exercised by one mineral form upon the other. For example cristobalite and tridymite occur in parallel intergrowth in the original specimens from Cerro San Cristobal.[9] The twinning edge of a tridymite trilling lies parallel to the octahedral edge of an octahedron of cristobalite. This brings the outside faces of the trilling nearly parallel with the octahedral faces of the cristobalite.

Properties of colored quartz

The best present evidence indicates that the color of most specimens of amethystine quartz is due to a compound of iron; that of most of the rose quartz, to a compound of manganese; and that of most of the smoky quartz, to silicon set free by the radiations from radioactive elements.[10] There are other causes of color, but they appear to be less important than the causes mentioned. In most instances the colors are irreversible destroyed by heat.

Some radiational properties of smoky and amethystine quartz

The particles which give the color and cloudiness to smoky quartz are submicroscopic in size. Sur[11] could not resolve them with the ultramicroscope method of Siedentopf & Zsigmondy.

[8] Article cited in IV, note [27].

[9] vom Rath, article cited in IV, note [35].

[10] See especially Holden, E. F., Amer. Mineral. (1924) **9**: 75-88, 101-108; (1925) **10**: 203-252.

[11] Sur, N. K., Proc. Indian Assoc. Cultiv. Sci. (1923) **8**: 271-275.

A yellow quartz from Madagascar also owes its color to some kind of submicroscopic inclusions, according to observations of its scattering power made by Strutt.[12] The polarization of the scattered light was nearly complete, the weaker image having but 0.007 the intensity of the stronger one. The stronger was bluish, but the weaker was a very rich blue; if this is the same as the "residual blue" observed by Tyndall in precipitated clouds, then the scattering particles are not small compared with the wave-length.

A slightly smoky quartz from Brazil gave less intense scattering than a yellow Madagascar quartz but of a good sky-blue color, indicating the presence of scattering particles. The polarization was about 97 per cent complete.

Refraction

The index of refraction of a solid containing transparent particles of submicroscopic size deviates from that of the pure substance by an amount proportional to the percentage by volume of the impurity. The amount of impurity in a smoky quartz is usually so small that no effect is noticeable in its indices of refraction. Some differences brought out by precise measurements have already been shown in Table XXXI. The value 1.560 given by Sur for N_ω of a smoky quartz examined by him must be in error, as the difference from the value for pure quartz is impossibly large.

Absorption

If the cloudiness or color is due entirely to the scattering of light by small particles, then smoky and yellow quartzes should be just as transparent to the ultra-red as visually clear quartz, because the scattering is effective in inverse proportion to the fourth power of the wave-length: $\lambda^4 \log (J_o/J) =$ constant (see XXXVI). Doubling the wave-length, say from deep red at 0.8 μ to near ultra-red at 1.6 μ, would thus reduce the scattering to one-sixteenth.

A specimen examined by Raman [13] was in fact found transparent to ultra-red. Koenigsberger [14] measured the transparency of brown smoky quartz at many points between wave-lengths 0.8 and 4.0 μ, and found the curve from 1.2 to 4 μ to be identical with that for transparent quartz, differing from it only in the region near the visible spectrum.

On the other hand the light-dissipating power of smoky quartz is not always due entirely to the scattering power of the finely divided substance which gives the color. This is shown by measurements by Sur,[15] using two different methods:

(a) Comparison of the absorption in the visible and ultra-red. The quantity $\lambda^4 \log (J_o/J)$, instead of being constant, was found to increase uniformly with wave-length from violet towards red, and then much more rapidly in the ultra-red, showing that in this specimen absorption accompanies scattering throughout the range.

[12] Article cited in XXXVIII, note [1].
[13] Nature (1921) **108**: 81.
[14] Article cited in XXXVI, note [8].
[15] Article just cited.

TABLE XLII.6.

PRINCIPAL ROCK TYPES CONSISTING OF PURE OR NEARLY PURE SILICA.

Principal characteristic	English name	French name	German name
ROCKS CONSISTING MAINLY OF QUARTZ.			
Compact, usually anhedral, evidently occupying clefts or lenticular openings, but not made up of cemented sand	Quartz vein	Filon de quartz	Kiesader Quarzader
Compact; evidently of sedimentary origin; recrystallized, or cemented with quartz which has grown in continuity with the original grains	Quartzite	Quartzite	Quarzit Quarzfels
Somewhat porous, of sedimentary origin; grains cemented with quartz or chalcedonic silica	Quartz sandstone	Grès	Quarzsandstein Kieselsandstein
Like sandstone, but in dike-like form	Sandstone dike		
Open-textured sandstone with angular grains	Buhrstone Burrstone Burstone Millstone	Meulière	Burrstein Mühlstein
Quartzite possessing a structure which renders the rock flexible	Itacolumite Flexible sandstone	Pierre élastique	Biegsame Sandstein Gelenkquarz
Compact; like quartzite, but with a cement of chalcedonic or of opaline silica	Cemented-quartzite		
ROCKS CONSISTING OF CHALCEDONIC, MICRO-AMORPHOUS, AND OPALINE SILICA.			
Compact; aphanitic or crypto-crystalline; produced by contact metamorphism	Novaculite	Novaculite	Wetzschiefer
Replacing and preserving details of wood fragments or logs	Fossil wood Silicified wood	Bois fossile Silex xyloide	Verkieseltes Holz
Porous, not cemented, consisting of micro-amorphous silica	Diatomite *	Randannite *	Kieselguhr *

* See also Table XLII.5.

(b) Comparison of intensities of scattered beams from smoky quartz and from a sulfur sol. If the dissipation of light in the quartz and the sol were both due to scattering alone, then the ratio of the scattered intensities J_q/J_s at a definite frequency would be equal to the ratio of the apparent absorption-coefficients k_q/k_s; the subscripts q and s refer to quartz and sulfur respectively. In the present case J_q/J_s is about 7 while k_q/k_s is nearly 42, indicating considerable true absorption.

Sur observed photographically that the specimen of smoky quartz on which he made measurements of scattering power was practically opaque to wave-lengths from the iron arc shorter than 290 mμ.

These different lines of evidence make it probable that his specimen, in addition to containing light-scattering particles, contained also coloring matter such as is found in amethyst. Koenigsberger examined an amethyst which showed strong absorption near 3 μ, although his smoky quartz was quite transparent to that wave-length.

Silica rocks

Out of the atom and molecule the chemist constructs his *chemical substance* (see Chapter I), which the mineralogist uses to build a *mineral*. A mineral may, and usually does, consist of a single pure substance; but it may also consist of a mixture or mechanical combination of substances in such constant manner of association that the combination must be taken as the unit. Chalcedony consisting of an inseparable combination of micro-crystalline and micro-amorphous silica is such a mineral.

The mineral is the unit out of which the petrologist constructs the *rock*, which in turn is one of the geologist's units of operation. A rock may, but seldom does, consist of a single mineral and is then called *monomineralic*. Silica forms a larger number of monomineralic rocks than any other substance.

Some of the more important rocks consisting of pure or nearly pure silica are listed in Table XLII.6.

Chapter XLIII. INDUSTRIAL APPLICATIONS OF SILICA

A classification of the uses of silica

The basis of all industry and trade is human desire for this or that particular duplicatable object, and that desire can be nearly always expressed in terms of the properties of the object, among which one property will be seen to overshadow the others. This property of the object, in turn, can be stated in terms of one or more properties of the substance (Chapter I) or substances of which the object is composed.

Conversely, a list of the properties of a substance can be made the basis for a list of the uses to which objects containing that substance can be put. Applying this procedure to silica, we find that two general divisions of the subject are immediately possible:

A. Chemical uses: those to which silica is adapted by virtue of the fact that its composition is SiO_2 and not Al_2O_3 or SiC. It serves as one component in a poly-component system.

B. Physical uses: those to which silica is adapted by virtue of the fact that it possesses some one desired property, usually with several others supporting it in a subordinate way. If the same property is possessed by Al_2O_3 or SiC they will do equally well.

Examples of class A are the use of silica as a constituent of glasses and slags; of class B, its use as an abrasive, as a refractory, as a material for lenses.

Our present interest in its chemical uses ends when it is delivered in a satisfactory form to the manufacturer or consumer. The technologist who is concerned with the poly-component system into which it enters,—the glassmaker, the acid manufacturer, the iron smelter,—may take it over at that point.

In its physical uses, on the other hand, it retains its individuality longer, and deserves some further attention in this summary. (Chapters XLV and XLVII.)

Before proceeding to these details we may devote a few pages to sources and manufacturing processes.

Industrial sources

Quartz is the form of silica principally used in industry. Chalcedonic silica and micro-amorphous silica are used in smaller amounts. Natural tridymite and cristobalite, on account of their mode of occurrence, have no industrial value.

Quartz

Quartz sand and gravel for use in cement concrete, mortar, and other constructional work make up the greater part of the tonnage of industrial quartz. For these purposes it is obtained as near as possible to the locality where it is to be used.

Most of the silica used for other purposes in the United States comes from sedimentary sandstone beds of nearly pure quartz in formations of Ordovician, Silurian, and Devonian age. In the Appalachian Highlands province of the eastern United States these Paleozoic formations have been folded into waves whose crests have subsequently been eroded away. The upturned edges of the hard sandstones now form long parallel ridges in the Appalachian Mountains, and outcrop thus from northern New Jersey through the middle Atlantic States to Alabama. In the States farther west these sandstones lie nearly horizontal.

In some localities the sandstones break down readily into quartz sand, and furnish this country's principal source of glass sand. More commonly, the standstone is so firmly cemented into quartzite that the outcrops resist weathering and yield great quantities of talus consisting of quartzite blocks of all sizes. These talus heaps are known locally as "ganister floes", and are the principal source of silica for refractory brick.

Sandstones of similar geologic age in the Ohio and upper Mississippi basins form another important source of quartz for abrasives and refractories, and to a smaller extent, for glass.

Chalcedonic silica

Chalcedonic silica comes to the market mainly in the form of chert nodules or water-worn flint pebbles. The principal source of supply has been the sea-coasts of England and France, where the weathering away of the limestones and shales has left large residual deposits of chert and flint.

During the past two decades a "flint famine" has threatened in England because of the exhaustion of the most easily available supplies and consequent rise of prices. This has caused other sources of silica to be considered among the possible raw materials for pottery bodies. The problem furnishes a good example of the many angles from which a change in technical procedure or raw material must be viewed.

Moore & Mellor[1] discussed several possible sources of silica to replace flint. Their principal substitutes are all of the nature of quartz, that is, well-crystallized silica, such as silica sand and quartzite. Quartz acts very different from flint in pottery bodies, for several reasons. It transforms to cristobalite much slower than flint (see XI); its reactivity with other substances, includ-

[1] Moore, B., & Mellor, J. W., Trans. Engl. Ceram. Soc. (1915) **15**: 103-109.

ing no doubt the clay and feldspar of the body, is less than that of flint; it is harder than flint, especially when the flint has been given a preliminary calcination, hence the same schedule of grinding produces a coarser silica; it is denser than flint, which brings about changes in the actual composition of the body if proportions have been measured by the volume of a slip.

A certain proportion of the added flint in a body may be rendered unnecessary by partially replacing one of the regular constituents with another which is higher in silica. Thus "Cornish stone" can be replaced with a more siliceous rock; and china clay or ball clay, with one of the more siliceous clays.

One important effect of using quartz, ground in the normal way, in place of flint, is said to be a considerable narrowing of the margin of safety with respect to crazing. On the other hand, if the quartz is ground extra fine, the loss from cracked biscuit is much increased.

Moore & Mellor also suggest chert as a substitute for flint in pottery bodies, but with the statement that such samples of chert as they had seen did not fire to a good color. Chert would have the advantage of behaving more nearly like flint than any other form or variety of silica (see XI).

A very different type of micro-crystalline silica is exemplified by the deposits found in Union and Alexander Counties in southern Illinois. It is so fine-grained as to be called "amorphous" but consists in reality of very fine-grained quartz.

The greater part of the silica beds consist of hard chert, which is quarried for road material. In much smaller bulk there occur thin bands of pure white soft silica which is mined for a variety of uses. The material contains over 95 per cent SiO_2 and is said to have run as high as 99.3 per cent. The greater part of the material consists of quartz grains less than 10 μ (0.01 mm) in diameter.

Rock crystal

Relatively very small in amount, but large in variety of uses and in technological importance, is the output of clear quartz crystals of "optical" grade. Almost all of the supply of this grade of quartz used in recent years has been "Brazilian pebble". It comes to the market in the form of water-worn fragments of originally euhedral quartz. The principal locality is near Diamantina, State of Minas Geraes, Brazil, where rock crystal has been formed by contact metamorphism[2] in a massive quartzite which is free from color-producing oxides, and has subsequently been transported down the river valleys as a result of weathering and erosion. The days of easily accessible river-bed deposits seem to be over, but geological exploration should be able to reveal additional supplies at the source.

Madagascar has also furnished good rock crystal during the past few years.

[2] WALLS, R. R., Trans. Opt. Soc. London (1920) **21**: 157-166.

The consumption of rock crystal for the manufacture of transparent vitreous silica (see XLIV) will probably increase steadily, and the day may be not far distant when optical quartz will be as much of a rarity as optical fluorite is at present. The art of communication by electromagnetic waves ("radio") will feel the effect also, because the demand for good quartz crystals for use in piezo-electric oscillators (p. 832) is beginning to be noticeable. Quartz may ultimately become a mineral of interest to internationalists, on account of its importance to the world's navies.

The remedy for the threatened famine is fundamental research on the conditions of growth of quartz, but such a research is likely to be time-consuming and commercially unprofitable.

Industrial preparation [3]

Crushing and grinding.—For most uses the raw silica as brought from quarry or mine requires to be crushed or ground. In descriptions of milling processes in connection with the preparation of silica no distinction is ordinarily made between true crushing and grinding which break up the crystals, and simple disintegration of an aggregate which consists of individual crystals more or less loosely held together.

The milling of the fine white silica of southern Illinois, for example, is probably mainly a mere disintegration process. The crystal grains are already extremely fine but must be mechanically separated. This is accomplished by grinding. Dry grinding is not so satisfactory as wet grinding, since it produces dust and yields an uneven product. The wet grinding is done in "chaser" mills, or in cylindrical tube or pebble mills. The product is then classified by being carried off in a current of water and allowed to settle.

The crushing of rock for glass sand is likewise mainly a process of disintegrating original sand grains which have been cemented.

The grinding of quartzite for refractory brick, on the other hand, is a true grinding process which breaks up the crystals.

Washing.—Another step which is sometimes necessary is the washing of sand or crushed rock to remove such impurities as clay or mica.

Burning.—Quartz and micro-crystalline silica are often subjected to preliminary burning. For this purpose rotary kilns have been widely used; also reverberatory furnaces with inclined hearths from which the material can be quenched; or shaft-kilns fired with gas or charged with alternate layers of quartz and a "clean" type of fuel such as charcoal or coke; or small reverberatory furnaces. Suitable temperatures for such burning have been found to be 950 to 1000°C. Such burning and quenching have the effect of breaking up the crystals by virtue of the 573° inversion

[3] An excellent detailed discussion of the technology of silica, about to be published, is: Weigel, W. M., *Technology and uses of silica and sand*, U. S. Bur. Mines, Bull. 266.

(see IX); if this be the only effect desired then a burning temperature of 600° should be just as effective as 1000°.

Silicosis

There is one aspect of silica in industry which deserves special mention, namely, the physiological effects of silica dust. These effects have long been noticeable in such places as the gold mines of South Africa, where deaths of miners from pulmonary tuberculosis became very common. It was supposed at first that the effect of the finely divided quartz breathed into the lungs was a mechanical effect, due to laceration of the tissues by sharp fragments whereby the lungs were made susceptible to such infections as tuberculosis. It is clear now that this is not the explanation, but that finely divided silica in the lungs is a kind of chemical poison. It is about the last substance on earth that the chemist would have suspected of being poisonous, for it is so universally distributed that we all eat it and breathe it all our lives. The subject has received careful attention within the past few years [4] and the industrial hazard will doubtless be brought under effective control.

[4] See especially reviews by SAYERS, R. R., Techn. Paper U. S. Bur. Mines (1925) No. 372, 24 pp.; and PANCOAST, H. K., & PENDERGRASS, E. P., Amer. Journ. Roentgenol. (1925) **14**: 381-423.

Chapter XLIV. THE MANUFACTURE OF VITREOUS SILICA

Vitreous silica became a commercial product,—one which can be and is made and sold at a profit,—at a comparatively recent date. In 1906 it was still a laboratory curiosity. Today it is being manufactured regularly in England, France, Germany, and the United States.

Vitreous silica is manufactured in two very distinct grades. The grade which I have called in this book *transparent vitreous silica,* often known as "fused quartz" (see p. 43), is transparent and free from bubbles and striæ; it is made by fusing selected quartz crystals. The grade which I have called *opaque vitreous silica,* often known as "fused silica" or by the trade name "vitreosil", is full of very small gas bubbles which have been drawn out into long tubes in the process of working, and the product sometimes has a silky appearance on this account. It is accordingly opaque or only translucent. It is made from quartz sand or some other finely divided form of quartz. Improvements in the technic of manufacture of this grade have increased its transparency considerably, and we may expect that the sharp distinction which now exists between the two grades will tend to disappear with progress in the art.

So far as I am aware, the electric resistance furnace is now universally used for the fusion of quartz on the larger manufacturing scale. The resistor is a graphite or carbon rod, tube, plate, or helix, and the charge of quartz surrounds or is contained within the resistor. Final form is given to the product by extrusion, drawing, or blowing, while it is hot enough to flow under stress, either immediately after the initial fusion or after the melt has been removed and then reheated. This is a very general description covering the commercially feasible processes. It should be noted that the method customarily used with ordinary glasses, of gathering a lump of the viscous liquid and then forming it, is not practicable with vitreous silica because of its high viscosity at workable temperatures. (See p. 473.)

Manufacture of opaque vitreous silica

In the process now generally used for the opaque or imperfectly transparent grade, the graphite or carbon resistor is surrounded by finely divided silica in the form of quartz sand or micro-crystalline silica. The temperature is rapidly raised and the portion next the resistor melts to form a crude cylinder or bulb. The apparatus is so arranged that the ends of the cylinder or bulb either remain fairly gas-tight automatically, or can be artificially closed. The gases, chiefly carbon monoxide, which

are generated around the resistor expand the viscous cylinder or bulb so that it is free from the resistor, which is then withdrawn. The unfused sand is allowed to fall away and the cylinder or bulb is thereupon quickly drawn into a tube, or it is blown, pressed, or rolled into the desired form. This must be done within a very short time, measured in seconds rather than minutes, before the glass becomes too viscous as a result of cooling. One of the discoveries made by Bottomley was the fact that if sufficient force or pressure is used to start flowage in the outside viscous skin, this skin is soon stretched and weakened so that the remainder of the operation goes much more easily.[1]

The process as described is operated by the Thermal Syndicate at Wallsend-on-Tyne, England; by the Deutsch-Englische Quarzschmelze at Pankow, Germany; by the Société Le Quartz Fondu at l'Argentière-la-Bessée, and a company known as Quartz et Silice, allied with the St. Gobain glass works, in France; and by the Sidio Company of America, in New York City.

Transparent vitreous silica

The transparent grade is made on a much smaller scale than the opaque and semi-transparent, for it utilizes a much more expensive raw material, namely, selected quartz crystals, and the price is correspondingly higher. The crystals are fused either in the electric resistance furnace or by the oxy-hydrogen or oxy-acetylene flame.

The General Electric Company's process [2] for transparent silica, operating at Lynn, Massachusetts, consists in fusion of clear quartz crystals in an electric resistance furnace which is evacuated. Such bubbles as are formed within the glass expand to large size and contain very little gas. They are compressed to negligible size either by rapid increase of gas pressure in the melting furnace, or by mechanical pressure in the subsequent step of the process, which consists in reheating the mass and extruding or drawing it into the desired form.

The manufacture of transparent vitreous silica by high-temperature flames will receive further mention at a later page. This process has been in use by W. C. Heraeus, at Hanau, Germany, and by the Hanovia Chemical & Manufacturing Company near New York City. These companies have probably also utilized electrical resistance heating.

A special process for transparent silica is that of the Silica Syndicate of London, now controlled by the Thermal Syndicate. It consists in building up a rod or other form continuously by keeping one end of it molten by means of an arc or an oxy-hydrogen flame while powdered

[1] For general descriptions see: Alexander-Katz, B., *Quarzglas und Quarzgut* (1919, Braunschweig), Sammlung Vieweg No. 46, 52 pp. Flusin, G., Chim. et Ind. (1920) **3**: 729-737; (1921) **5**: 119-135, 257-270. Paget, R., J. Roy. Soc. Arts (1924) **72**: 323-336.

[2] Berry, E. R., Gen. Elec. Rev. (1924) **27**: 369-373; Trans. Amer. Electrochem. Soc. (1924) **45**: 511-521.

silica is fed into it from above. The process is like that used for making artificial rubies (Al_2O_3).

Early development of the processes

Although quartz had been fused on a number of previous occasions (see VI), the first scientist to record an interest in the peculiar properties of vitreous silica was Gaudin,[3] who exhibited specimens of the glass before the Paris Academie in 1839 and gave an account of his experiments in fusing rock crystal with the oxy-hydrogen flame.

For sixty years it remained little more than a scientific curiosity, although its low thermal expansion and its insolubility in acids should have made it a subject of lively interest to physicists and chemists. About 1899 active experiments looking toward its commercial manufacture were begun in England, France, and Germany, with the result that by 1910 an industry of considerable importance, both to industry and to science, had been established in all three countries.

In 1869 Gautier[4] made some small tubes and air thermometers of vitreous silica which were exhibited at the Exposition Universelle of 1878, but the attention of physicists does not seem to have been generally attracted to the material until Boys,[5] in 1887, demonstrated its usefulness as a material for suspension fibers for galvanometers and the like.

At the time of Gautier's exhibit, however, Abbe seems to have perceived the possible usefulness of this new type of glass. He and Schott experimented about 1888 in the direction of making commercially usable optical vitreous silica but without much success. In 1890 Brun made similar experiments which were reported to the firm of C. Zeiss, but without developing into a commercial product or method. Parsons fused some quartz in an electrical resistance furnace in 1888, but as he was interested primarily in the development of the furnace, this more or less incidental product was laid aside.

About 1899 Heraeus, the German platinum manufacturer, and Herschkowitsch, who was associated with C. Zeiss and the glass manufacturers Schott & Genossen, both succeeded in manufacturing optical silica as a commercially feasible product.

Herschkowitsch[6] made the glass by first heating selected quartz crystals to about 500° in a carbon crucible, and then placing the material quickly in an electric arc furnace already heated to white heat. In this way the inversion point at 573° was passed through rapidly and with a distribution of stresses in the crystal such that the difficulty due to cracks and resulting bubbles was minimized. The Zeiss works exhibited optically homogeneous plates of the glass, 40×10 mm in size, at the Paris Exposition of 1900.

At about the same time Heraeus[7] made a considerable quantity of the glass from large quartz crystals by fusing them in an iridium vessel by means of a large oxy-hydrogen flame. With the aid of the firm of Siebert & Kühn in

[3] Articles cited in VI, note [35].
[4] Gautier, A., Compt. rend. Acad. Paris (1900) **130**: 816.
[5] Articles cited in XXIII, note [26].
[6] Article cited in V, note [39].
[7] Heraeus, W. C., Zeitschr. Elektrochem. (1902) **8**: 861-862; (1903) **9**: 847-850. Ber. Int. Kongr. Angew. Chem. (1903) **1**: 708-715.

Cassel, Germany, Heraeus then produced tubes and bulbs and apparatus of various kinds, which were exhibited at the International Congress of Applied Chemistry in 1903.

While this progress was being made in Germany, two independent investigators were making similar experiments in England and France. Dufour [8] reported his experiments to the Paris Academie in 1900, and Shenstone [9] published several reports in English periodicals.

At 573° quartz crystals are likely to splinter and fly to pieces if rapidly heated, because of the sudden change of dimensions due to the high-low inversion (Chap. VII). To avoid this difficulty, which makes quartz hard to fuse into a single lump of glass, both Dufour and Shenstone followed the plan of first heating small fragments to about 1000° and throwing them into water. The crystal under this treatment breaks up into such fine fragments that they hold together as a white enamel-like lump which can then be heated in the oxy-hydrogen or oxy-gas flame without splintering.

These fragments were fused in the flame in such a way as not to inclose bubbles of gas, and were then built up in succession until a rod or other form was produced. Dufour [10] reported that one hour's work sufficed to build up 4 or 5 rods about 30 cm long and 2 mm in diameter.

Heraeus did not have much success with Shenstone's method of first quenching the quartz crystals from 1000°, and preferred to heat the crystals up directly in the iridium container, entraining fewer bubbles in this way than by Shenstone's method. The rapid production of a vitreous film, which covers the outside of the crystal and helps to keep air out of the cracks, is an important feature in this procedure, as well as in that of Herschkowitsch.

Electrical methods

Meanwhile, Threlfall (1899) and Hutton (1902) had melted quartz in the carbon arc. Hutton fused crushed quartz into plates, rods, and tubes, holding the charge in a mold of artificial graphite, while the arc was either used in the open and deflected magnetically toward the quartz, or was used inside a Moissan furnace. Kent & Lacell (1910) patented a method of feeding powdered quartz into an arc, and others have made various adaptations of arc fusion, but without leading to a commercial large-scale process.

The successful type of electrical fusion, using a resistor instead of an arc, began with the experiments by Parsons in 1888, already mentioned, and was followed up by Elihu Thomson in the United States, Hutton and Threlfall in England, and Ruhstrat in Germany. Continuation of this work by Bottomley and Paget led in 1904 to the accidental discovery of the method of interior expansion by the generated gases, which is now the basis of the successful manufacture of opaque vitreous silica. Patents on modifications of the process were granted to Völker and others but the Bottomley-Paget patents held the field.[11] The early patents have now expired.

[8] Compt. rend. (1900) **130**: 775-776, 1753-1754.
[9] Nature (1900) **61**: 540; **62**: 20-22; (1901) **64**: 126.
[10] Journ. de Physique (1903) (4) **2**: 498-507.
[11] Zeitschr. Elektrochem. (1913) **19**: 760-771.

Use of pressure

Day & Shepherd [12] improved on the technic of manufacture of transparent silica by first utilizing the vapor of the silica itself to drive out air from between the grains or fragments, then applying air pressure to compress such small bubbles as might remain, and finally cooling under pressure. As actually carried out the process consisted in heating quartz sand rapidly to a temperature estimated to be above 2000°, in a graphite trough through which passed a heating current. When the silica was vaporizing freely an air pressure of about 35 atmospheres was applied, and the temperature was lowered to about 1800° where it was held about half an hour. The pressure was then gradually withdrawn during cooling.

The product consisted of clear blocks of vitreous silica about $7 \times 12 \times 1$ cm, with only a few bubbles, but with occasional slight discolorations of elemental silicon. An important new feature of Day & Shepherd's procedure is the device of squeezing the bubbles out of existence by external pressure. This has subsequently been re-invented and patented.

Devitrification of special types of vitreous silica

The devitrification of pure silica has been discussed in Chapter VI. A few notes may be added here on the devitrification of some special commercial types.

Attempts have been made to decrease the devitrifying tendency of vitreous silica by adding small amounts (less than 1 per cent) of TiO_2 or ZrO_2. The attempts have apparently not been successful. The weight of evidence is that these glasses devitrify even more rapidly than pure silica.

Special glasses of this kind were introduced by the Zirkonglas-Gesellschaft of Frankfurt, Germany, under the names "Titanglas" and "Zirkonglas" or "T-Siloxyd" and "Z-Siloxyd," containing 0.1 to 2.5 per cent of the oxides TiO_2 and ZrO_2. Devitrification tests were made in 1911 on tubes of these glasses by Thomas,[13] by heating them for 1 to 2 hours at temperatures of 1350 to 1500° in a carbon-tube electric furnace and measuring the thickness of the cristobalite layer. Although somewhat variable, the results were interpreted as indicating that both of the special glasses, particularly the one containing TiO_2, devitrified less rapidly than pure silica in the form known as "vitreosil".

Seger & Cramer [14] made similar comparisons between "vitreosil", "Titanquarzglas" (0.0 to 0.11 per cent TiO_2) and "Zirkonquarzglas" (0.05 to 0.15 per cent ZrO_2). The SiO_2 content was 98.5 to 98.9. Tubes about 2.5 by 20 cm were heated at 1550°C for 1 to 6 hours. The TiO_2-bearing glass seemed to devitrify fastest, the ZrO_2-bearing next, and the vitreosil least, but the authors state their belief that differences of the order of magnitude found by them are likely to result merely from accidental variations in manufacture.

Rieke & Endell [15] found that under most conditions these special glasses

[12] Day, A. L., & Shepherd, E. S., Science (1906) **23**: 670-672.
[13] Thomas, F., article cited in VI, note [46].
[14] Article cited in VI, note [45].
[15] Article cited in VI, note [37].

devitrified to cristobalite just as fast as, or faster than, "vitreosil" or "sidio III", both of which are semi-transparent varieties of fairly pure vitreous silica. The special glasses devitrified much faster than pure transparent vitreous silica made from quartz crystals.

The only exception to this order was found in tests on powders heated 5 hours at 1300°. The percentage of cristobalite, as estimated from pyknometer density, varied from 2 to 8 per cent, "sidio III" and "vitreosil" giving less than either the pure transparent glass or the TiO_2- and ZrO_2-bearing glasses. But with so small a percentage of conversion the results are uncertain, since they may be unduly affected by varying proportions of very fine dust in the powdered glass (see p. 98).

Michie [16] made comparative tests on "vitreosil", "Titanglas" containing 0.25 per cent TiO_2, and "Zirkonglas" containing 0.4 per cent ZrO_2. At 1550°, in an electrically heated carbon-tube furnace with a vitreosil lining, and again with an Acheson graphite tube inside the vitreosil, the two special glasses were found to devitrify appreciably faster than vitreosil. Furthermore, special glasses containing 0.6, 1.1, and 1.9 per cent TiO_2 were found to devitrify the faster, the greater the percentage of TiO_2. Similar results were obtained at 1250 to 1300° in a gas-works furnace, the glass with 1.9 per cent TiO_2 being completely white from devitrification when the vitreosil had hardly become affected externally. Michie suggested that Thomas' results might have been influenced irregularly by the vaporization of alkaline substances from his unprotected carbon heating-tube. This seems a reasonable explanation in view of the known effects of impurities (p. 98).

[16] Article cited in VI, note [47].

Chapter XLV. SILICA REFRACTORIES

One of the most important of the "physical" uses of silica (see XLIII) is its use as a refractory at high temperatures. The particular properties which recommend it for this purpose are: primarily, high melting temperature (pp. 41, 86); secondarily, good mechanical strength (p. 480), good abrasion-hardness (p. 493), relatively low thermal conductivity (p. 416), very low electrical conductivity (p. 527). In addition, its abundance and accessibility give it an advantage over other oxides which equal or exceed it in thermal refractoriness.

The ideal silica refractory for long-continued use at a constant temperature would be a refractory made of pure quartz if the temperature were to be below 870°C, of pure tridymite if between 870 and 1470°, or of pure cristobalite if above 1470°. Such a refractory would remain absolutely unchanged except by external corrosion, for the inversion points are unchanged by the presence of other substances.

Aviators tell us that traveling through the air is simplicity itself, that getting off the ground and getting back to it are the only parts of the journey requiring much skill. So with the refractory: although it may stand a long-continued high temperature without harm, it is likely to be severely tried when heating up and cooling down. The principal source of trouble comes from the high-low inversions (Chap. VII), each of which is accompanied by a sudden change of dimensions in the crystals of silica. From this point of view tridymite is preferable to cristobalite or quartz, because the two inversions in tridymite are accompanied by very small volume-changes (Chap. XX).

Now that the ranges of stability of the modifications are known (Chap. IV), and that at least partial information concerning rates of transformation is available (Chap. V), it is technically if not economically possible to make a refractory whose silica is all of a single modification. The presence of more than one modification means instability and continuous change.

For use above 870°C the presence of quartz is considered undesirable because of the large expansion in passing from quartz to either of the other two forms. In the ideal case the conversion of the quartz into one or other of the high-temperature forms, cristobalite or tridymite, should be as nearly complete as possible before the refractory is built into a furnace. Conversion going on after the refractory is in place may cause permanent expansion, putting stresses into the structure and causing spalling or breakage.

Refractory brick

Silica employed as a refractory is almost always used in the form of bricks of various shapes and sizes. There are manufactured by crushing or powdering the silica, mixing it with a sufficient amount of some other material, usually lime or clay, to act as a bond, and then heating it at a high temperature. These two important operations of powdering and heating are known technically as the "grind" and the "burn", respectively.

There are two principal types of refractory siliceous brick. These are:

(A) *Silica brick,* which consists of nearly pure silica with a little lime (CaO) as bond.

(B) *Quartzite brick,* which contains less silica than (A), and is made with clay as bond.

Most of the discussion in this chapter will have reference to silica brick rather than quartzite brick.

The raw material is always quartz, sometimes containing chalcedonic silica as an accessory mineral.

Manufacture of silica brick

The process of manufacture of silica brick consists of the following principal steps: Grinding (with addition of lime); molding; drying; and burning.

Grinding.—In American practice the grinding is nearly always done in a wet pan, and the lime is added during the grinding. The ground silica contains particles from about 4 mm diameter down to micro-sizes, such as remain in suspension in water. The shape and size of the brick and the use to which it will be put are deciding factors in the control of the fineness and the distribution of sizes. Thus a larger proportion of fine material is used for special shapes than for the common 9-inch brick.

Experience has shown that the percentage of CaO in the finished brick should be between 1.5 and 3.0. If the percentage is less than 1.5 the brick is found to be too weak; if over 3.0, it is said to lose in refractoriness, but recent evidence throws doubt on this conclusion.

Molding.—Silica brick are molded to dimensions smaller than those of the finished brick in order to allow for the expansion during burning. The usual allowance is $\frac{3}{8}$ to $\frac{7}{16}$ inch per foot, that is, about 3.1 to 3.6 per cent, equivalent to 9.3 to 10.8 per cent in volume. Pure quartz expands 14.3 per cent in volume when changing to cristobalite (XX).

Burning.—In American practice, the burning temperature for silica brick is about 1450°C and the time of burning about 20 days. In terms of Seger cones, the burning temperature usually called for is cone 15 to 16 or cone 16 to 17.

The changes that take place in the silica during burning can be predicted from the facts set forth in Chapters IV and V. Cristobalite is the

first product, which then changes to tridymite if the temperature does not exceed 1470°.

Influence of constitution of raw material

The facts set forth in Chapter XI throw light on the effects of one type of variation in the raw material, namely, the character of its crystallization. A brick made of coarsely crystalline quartz requires either a longer time or a higher temperature for its conversion than does a brick made of finely crystalline quartz, chalcedonic silica, or amorphous silica. Hence with a given expenditure of heat a more thoroughly converted brick can be made from a quartzite containing the latter varieties of silica than from one containing coarse-grained quartz.

Experience in Germany showed very early that silica brick made from the massive Devonian quartzite of the lower Rhine region were less satisfactory than silica brick made from certain quartzites of Tertiary age, which are classed as "cemented-quartzites". This Tertiary quartzite is usually obtained, in Germany, in the form of loose blocks or boulders formed by the natural weathering and breaking down of the quartzite beds. It contains a considerable proportion of chalcedonic silica, which is transformed much faster than massive quartz.

Fine grinding

As might be expected from the data in Chapter XI, the disadvantage of coarse crystallinity in its effect on rate of conversion of the quartz into cristobalite can be offset by fine grinding.

Before the European War of 1914 German silica brick were sold in England in active competition with British-made brick. This was made possible, at least in part, by the fact that the Germany chalcedonic raw materials could be converted much more rapidly into cristobalite than could any type of coarsely crystalline quartzite, and better results could therefore be obtained with a given expenditure of heat.

The War, by not only cutting off German importations but also greatly increasing the demand for silica brick for steel making, forced British manufacturers to develop fine grinding as an aid to the conversion of quartz into cristobalite. American manufacturers, who had always been dependent on coarsely crystalline quartz as their raw material, had already developed this art in their procedures for making silica brick. As has happened so often in the history of technology, necessity has been not only the mother of invention but the grandmother of unforeseen technical progress, and much of the American silica brick is now of better grade than the German, in spite of the fact that the raw material is more difficult to convert.[1]

[1] Endell, K., J. Amer. Ceram. Soc. (1921) **4**: 953-960.

Purity of raw materials

The best silica content for rock to be used in making silica brick, according to American experience, is from 96 to 98 per cent. Either a smaller or a greater percentage of silica is not so satisfactory.

The importance of the impurities lies in their effect in accelerating the transformations of silica (see V). At the same time, they form lower-melting compounds and eutectics which weaken the brick at a temperature where the compound or eutectic is liquid.

The composition of the 2 to 4 per cent of impurities therefore affects the suitability of the rock for making silica brick. The percentage of Al_2O_3 should not exceed 2.5. The total alkaline oxides (Na_2O and K_2O) should be less than 0.5 per cent. The percentage of Fe_2O_3 is probably of less importance.

Another feature of the impurities is their distribution. One reason why better bricks are obtained from the cemented-quartzite, as emphasized by Endell,[2] lies in the distribution of its impurities. In a true quartzite they are usually segregated in relatively large units, such as mica crystals, for example. The impurities in a cemented-quartzite, on the other hand, have been held by adsorption in the deposit of cementing silica; they are very finely divided and uniformly distributed through the cement. On burning, the relatively large micas or other impurities in the true quartzite have little effect on the rate of conversion, and may become a source of weakness in the brick by their decomposition or fusion. The finely distributed impurities in the cement of the cemented-quartzite, on the other hand, may aid in hastening the conversion into cristobalite, since such impurities usually act as centers where recrystallization of the silica commences.

Character of the bonding

During the burning the natural impurities and the added lime in a silica brick form silicates which liquefy at various temperatures and penetrate by capillarity among the grains of silica. On cooling these silicates solidify to glasses or fine-grained crystalline aggregates, cementing the grains together, just as they do in ordinary red brick and numerous other ceramic products. These products, however, are used at atmospheric temperatures. The silica brick must maintain its strength on returning to high temperatures where the cement is again liquefied. More stringent requirements must therefore be made of the bond in a silica brick than in most ceramic products. Preferably it should consist of a cohering intergrowth of the silica itself.

This is a problem that invites fundamental study, involving rates of crystallization, mutual influences in the orienting of crystals, cohesion of unoriented and oriented crystals, and allied questions.

[2] Endell, K., Stahl u. Eisen (1913) 33: 1770-1775, 1855-1860.

If the brick is to be made of quartzite, American experience indicates that a rock which crushes into splintery, angular fragments of non-uniform size and shape is the best. Rock which crushes into rounded grains does not give as satisfactory results. We may imagine that this is because the angular fragments make better contact with each other on account of the nearer approach to planeness in their faces.

Le Chatelier[3] has published photographs of thin-sections of quartz sand that has been heated at 1700° with various fluxes. These sections show how the quartz, changed to cristobalite by the high temperature, has dissolved around the edges of the original grains and then recrystallized out of the melt again as cristobalite. He suggests that this process, in the presence of a smaller amount of flux than was used in his experiments, would effectively bind together the original grains, and that this is probably the principal source of strength of a silica brick.

Changes during use

The changes that occur in a silica brick when used for a long period at constant temperature depend primarily on that temperature, and secondarily on the chemical environment. The silica changes entirely to tridymite if between 870 and 1470°C, and to cristobalite if between 1470 and 1710°, and it melts if above 1710°. Volatilization and dissolution of the silica, and removal or addition of impurities, also take place.

If the temperature fluctuates above and below 1470°, the effects are not so easy to predict. The rate of transformation of cristobalite to tridymite and the rate of the reverse transformation vary with temperature. They also depend upon the size of the crystals and the area of their free surfaces, variables which in turn depend upon the previous thermal history of the brick. Furthermore, the rate is influenced by the manner of distribution of the impurities, which may change with both time and temperature. If we knew how each of these variables depended upon temperature and time, we could write an exact equation for the amount of tridymite or cristobalite which would result from a given thermal history of the brick.

In the course of long exposure in a steel furnace, a silica brick tends to develop three distinguishable zones.[4] The first zone, exposed to the hot gases, is found to consist of a mixture of cristobalite and vitreous silica, or it may be almost wholly cristobalite if the brick has cooled slowly and if there is not so large a quantity of impurities present that considerable amounts of complex silicate glass remain.

The second zone consists almost wholly of tridymite crystals. The presence of tridymite indicates that this portion has stood during considerable periods at a temperature between 1470 and 870°. It does not

[3] Compt. rend. Acad. Paris (1916) **163**: 948-954.
[4] Endell, K., Stahl u. Eisen (1912) **32**: 392-397.

mean that this portion has never been above 1470°, however. The final result is a balance between two alternating inversions, and is an integrated effect of both the time and the relative rates of transformation.

Of both zones it is fair to say that the net result of summing up time and temperature below 1470° and time and temperature above 1470° usually comes out greatly in favor of tridymite for the second zone of the brick and in favor of cristobalite for the first zone. It is conceivable that the second zone may actually have been above 1470° for a much longer time than it was below 1470°, and yet the relations between the rates have been such that the second zone is mainly tridymite. The actual times and temperatures are not revealed by the compositions of the zones.

The third and outer zone is rather different in character from the other two. It represents a portion of the brick which has suffered comparatively little change, because it has never become hot enough to permit the various possible reactions to occur at an appreciable rate. It still contains fragments of quartz which existed in the brick when it was first set in the furnace.

The formation of new quartz in this zone, which might conceivably take place if its temperature stood for a while below 870°, has not been reported. The probable causes for this are, first, the fact that quartz never forms by the "dry" heating of pure silica; second, the fact that below 870° the impurities usually found in a brick are either not fusible or are not liquid enough to form an active flux in which quartz could grow.

The boundary between the cristobalite and tridymite zones is sometimes quite sharp. Holmquist [5] has observed it as a sharp boundary under the microscope, in a thin-section of brick cut perpendicular to the heated surface.

The transition from the second to the third zone is marked by unchanged quartz fragments and by fragments of quartzite changed to cristobalite but bordered with tridymite.[6]

Some investigators distinguish four or even five zones.

Sokolov [7] has followed the transformations in silica brick by examining thin-sections of brick from the walls of steel-furnaces. Crystallization begins first in the fine-grained interstitial material, yielding crystals of tridymite. The larger grains of quartz begin at the same time to transform on their outer surfaces to an isotropic material, and also break up into smaller and smaller fragments. Ultimately the quartz area becomes entirely isotropic, then faintly birefringent, then finally transforms into tridymite. Meanwhile the tridymite in the interstitial areas has grown larger, keeping ahead of that formed from pure quartz. The net result at this stage is a fairly uniform crystalline ground-mass in which finer-grained areas stand out representing original quartz grains.

[5] Article cited in V, note [9].
[6] Endell, K., article cited in note [4].
[7] Sokolov, V. I., Proc. Imp. Mineral. Soc. St. Petersburg (1906) **44**: 473-482, pls. 8-9 (Russian).

Although not actually correlated with temperature and time of exposure, the persistence of the original texture enables the course of the transformation to be followed in a series of microscopic sections, much as the biologist correlates his stages of cell-development by means of slides which may even be taken at random.

Grum-Grzimailo[8] made microscopic examinations of silica brick from several Russian steel works, including some experimental bricks, and concluded that the essential reaction is the conversion of quartz into tridymite at a rate slow enough to permit the formation of a well-knit structure of tridymite crystals. The disintegration caused by too rapid heating he ascribes to too rapid conversion of the quartz, finding that a badly disintegrated brick and another which had given several months' service in a Martin furnace both had the same specific gravity, namely 2.33. He pointed out the important role played by finely divided impurities in the original raw material, in forming liquid silicates and thereby accelerating the transformation.

Observations on silica brick from the crowns of glass furnaces are entirely in accord with the facts and principles already stated. Ferguson & Merwin[9] found that brick from the crown of a glass furnace heated regeneratively, in which the direction of air and gases was reversed every 15 or 20 minutes, contained good crystals of tridymite. Evidently the brick had been at a temperature below 1470° during at least a part of each cycle.

Brick from the crown of a glass furnace heated recuperatively, in which the flame played continuously on the brick, and so placed that it was not cooled by leakage of cold air from the furnace door, contained mainly cristobalite. This brick was undoubtedly kept at a higher average temperature than the brick from the regenerative furnace.

The formation of tridymite in a brick takes place more rapidly in the fine-grained interstitial material than in the larger grains which were originally nearly pure quartz.[10] This is probably the result of the formation of a small amount of liquid silicate from impurities in the interstitial material, this liquid then acting as a flux to accelerate the growth of tridymite crystals. The quartz areas, when completely converted to tridymite, are more transparent than the original grains, and the impurities in the quartz become segregated.

Le Chatelier[11] has published photographs of thin-sections of silica brick taken by Hadfield from Bessemer converters and open-hearth furnaces. The silica in Bessemer brick was mostly cristobalite; in the open-hearth brick, mostly tridymite. Le Chatelier interprets this to mean simply a more rapid crystallization of the silica of the Bessemer brick, but I believe it is better explained by the general principles just discussed.

[8] Grum-Grzimailo, W., article cited in V, note [64].
[9] Article cited in V, note [2].
[10] Holmquist, P. J., article cited in V, note [9].
[11] Bull. Soc. Franc. Min. (1917) **40**: 44-57.

Volatilization

Blasberg cites evidence that there is considerable volatilization of silica from the bricks of steel furnaces. Endell [12] found that the fused cristobalite-bearing zone, 2 to 3 cm thick, contained only 90 per cent of SiO_2; this may indicate concentration of the original impurities, or it may result from the addition of impurities in the form of dust from the furnace gases, so that it does not necessarily prove volatilization.

The loss of silica by direct volatilization from the surface of silica brick is probably aided by the reducing action of the gases (see p. 107), as well as by the reducing action of carbon found diffused through the hotter zones of the brick. How the carbon is deposited there is not known, but Blasberg and Endell have both shown that it disappears after long-continued heating at high temperatures.

Historical notes

The first silica brick were made by Young in 1822, from the so-called Dinas sand in Wales, and so gained the name "Dinas brick" which has come to be used by some writers as a generic term for all types of silica brick.

The expansion or "swelling" (German *Wachsen*) during the use of silica brick has been a troublesome characteristic from the time they were first used in steel furnaces down to the present time. Its explanation as being due to a continuing inversion of one form of silica into some other form suggested itself to the early investigators, but could not be confirmed for many years. Mallard's discovery in 1890 of tridymite crystals in a long-used silica crucible suggested that the inversion of quartz to tridymite might be the cause of the swelling. The suggestion was generally overlooked until revived independently in 1901 by Cramer.

The presence of cristobalite in silica brick was first demonstrated by Holmquist [13] in 1911. The fact that nearly all of the inversion-product of the quartz in the brick is cristobalite was not immediately recognized, however, because the fine-grained condition of the main mass of cristobalite made it appear optically isotropic (see p. 602). Both Holmquist and Grum-Grzimailo therefore supposed that the initial product was amorphous or vitreous silica, from which both tridymite and cristobalite subsequently grew.

Le Chatelier,[14] at about the same time, suspected that a variety of silica which he had observed in Dinas bricks, and which had an inversion at 215°, was identical with cristobalite, but he was deterred from publishing this conclusion as final because of Mallard's statement that the cristobalite inversion takes place at 175°. Le Chatelier simply called the unknown form "silice X." In 1916 he recognized the identity as proven, through the work of the American and German investigators of the cristobalite inversion.

During the past decade, the importance of silica as a refractory material for furnaces has made it the subject of much study in laboratories allied to the

[12] Article cited in note [4].
[13] Article cited.
[14] Rev. univers. mines (1913) (5) 1: 85-142.

ceramic industries, such as those of the Harbison-Walker Refractories Company, the U. S. Bureau of Standards, and the U. S. Bureau of Mines.[15]

Molding sand

Another very important use for silica in the form of quartz sand should be mentioned here, although, strictly speaking, it is not an application of pure silica. In the mineral statistics "sand" includes not only pure quartz sand but also products containing varying amounts of clay and other admixtures: these products are consumed mostly in the making of molds for casting iron and other metals. Their total tonnage stands second only to building and paving sand in magnitude. The clay or other impurity is necessary as a binder to give strength to the mold, while the distribution of sizes among the sand grains is highly important because of the necessity for porosity in the mold to permit of the escape of gases. Some fundamental research bearing on these problems has recently been undertaken by a group of cooperating organizations in the United States.

[15] See, for example, general articles by: McDowell, J. S., Trans. Amer. Inst. Mining Eng. (1916) 57: 3-61: Ross, D. W., U. S. Bur. Standards Techn. Paper No. 116 (1919) 84 pp.: Insley & Klein, same, No. 124 (1919) 31 pp. Also papers by Rees, Endell, Le Chatelier, and numerous others in English and Continental technical periodicals.

Chapter XLVI. CHEMICAL USES OF SILICA

In Chapter XLIII the "chemical uses" were defined as those into which silica enters as one component in a poly-component system. The following are five important types of systems in which the chemical properties of silica are of value:

A. Commercial fused or agglomerated silicates: glass, slags, clay products.

B. Commercial solutions of silicates: water-glass.

C. Liquid phases in which silica is highly insoluble: water, acids.

D. Liquid and gaseous phases from which particular substances can be absorbed: oils, mixed gases.

E. Systems in which silica is reduced to elementary silicon.

(A) use in fused silicates. *Glass*

Quartz sand is the form of silica almost exclusively used for making silicate glasses. Its percentage by weight in the finished glass varies from 40 to 85 per cent, depending on the type. It is greatest in "Pyrex" glass and lowest in the heavy lead glasses.

For common bottle glass an impure sand, such as can be found in almost any locality, is entirely satisfactory, but for the better grades of glass, in which it is important that there shall be no noticeable color, a fairly pure grade of silica must be used. Oxides of iron are the most troublesome impurities, and the percentage of Fe_2O_3 is usually held to 0.1 per cent or less, but the percentage of SiO_2 may be relatively low, less even than 90 per cent, because if color-producing impurities are absent the other oxides, such as CaO and Al_2O_3, can be allowed for in making up the "batch" or mixture of raw materials.

The physical state of the sand is also important. The size of grain should be uniform, and should lie between the limits 0.1 and 0.5 mm. Angular grains are preferred to rounded grains.[1]

Calcined flint (p. 794) was used in the seventeenth century for making the best grades of glass, especially lead glass. This use ceased long ago, but the name "flint glass" still persists. The word "flint" has also been carried over in ceramics as a technical term almost synonymous with "silica" and so including quartz, but in the sciences the word is now restricted to mean impure dark-colored micro-crystalline silica (Chap. X).

[1] General articles: Colony, R. J., N. Y. State Mus. Bull. 203-204 (1917) 31 pp. Fettke, C. R., Top. Geol. Surv. Pennsylvania, Rep. 12 (1919); Cole, L. H., Canada Dept. Mines, Mines Branch, Publ. 555 (1923) 126 pp.

Enamels for use on metals form another type of glassy silicate for which silica is a raw material. The requirements as to purity are like those for glass, but the material is used in a finely ground condition.

Slags

Silica is an essential constituent of many of the slags used in metallurgical processes. For this use a molten silicate which is quite fluid is desired. Hence the percentage of the highly viscous constituent silica is much lower than in glasses, and is only about 30 to 40 per cent of the total. Chemical purity of the silica is not of such importance as it is with silica for glass.

Clay products

In glass, enamels, and slags the silica is an essential constituent which has to be mixed with the other raw materials. In wares made of clay, on the other hand, the added silica sometimes has more the nature of a space-filling material; the grains can still be seen in the finished product, although united by fusion with neighboring silicates. Nevertheless it must be considered a chemical constituent, because the combination of free silica with the other silicates often proceeds to the complete disappearance of silica as such.

In common brick, common stoneware, terra cotta, and sand-lime brick most of the quartz sand which is present or added may undergo no change. In vitrified products, on the other hand, it may fuse partially or entirely with the fluxing constituents and become part of a silicate.

Chalcedonic silica in the form of flint and chert has been used much longer in the clay-product industries than in glass-making, particularly in England. For this use it is usually calcined, and probably undergoes partial transformation into cristobalite if the temperature becomes high enough (XI).

In other countries quartz has been more used than chalcedonic silica. Crushed vein quartz and natural quartz sand have both been employed in German porcelain manufacture, and technical practice in their use has varied greatly. The replacement of the one by the other has been a favorite subject of discussion in the technical ceramic periodicals. Part of the difference in results, assuming always equal chemical purity, has no doubt been due to different degrees of fineness in the preparation of the material. Another source of difference not so commonly recognized is the possibly different constitution of the quartz as regards twinning, strain, and gas inclusions, all of these being factors which influence the fineness of subdivision on heating (XI) and hence the fusibility or the rate of dissolution in other silicates.

Micro-amorphous precipitated silica, also, has been tried in clay products. Its greater speed of reaction as compared with the crystalline

modifications (p. 80) appears again in its reactions with silicates. When used to replace quartz in porcelain bodies, for example, it causes greater shrinkage, and, if carried to higher temperatures, earlier fusion.

(B) Use in soluble silicates

The commercial soluble silicates are sodium silicate (water-glass) and potassium silicate. When made by the dry process, quartz sand or crushed quartz is melted with the alkali carbonate (or with sulfate and carbon), and the melt is afterwards treated with water.

In the wet process chalcedonic silica and micro-amorphous silica are preferred. Ground flint or diatomite are digested with a caustic alkali solution until dissolved. The greater surface per unit weight and the more rapid rate of reaction (p. 80) are the desirable qualities of the micro-forms as compared with quartz.

For these products a fairly pure grade of silica is required, but the necessity for freedom from color-producing oxides is not as stringent as with high-grade glasses.

(C) Uses depending upon insolubility

Both quartz and vitreous silica are prized for their insolubility in water and acids,—or perhaps one should say their slow rate of dissolution, for nothing certain is known of their true solubility.

It is this property which combines with abundance and accessibility to make quartz sand the preferred material for making filter beds for the filtration of municipal water supplies and municipal sewage. A sand with the proper distribution of grain sizes is desirable for this use and one fairly high in silica, while the color-producing impurities are unimportant.

The use of quartz sand as an outer coat in various kinds of roofing also belongs in this class.

For filling acid towers, such as the "Glover tower" in the manufacture of sulfuric acid, crushed quartz of fairly coarse grain is preferred, since liquid films traveling in one direction are to be exposed to gases traveling in the opposite direction.

For the handling and concentration of acids, vitreous silica in the form of flasks, basins, spouts, and pipes, has become a very useful materia within the past fifteen years. It was this use that made possible the establishment of the opaque vitreous silica industry in England (XLIV) In the manufacture of sulfuric acid, silica has displaced the highly expensive gold and platinum stills and the unsatisfactory glass stills formerly used for concentrating pure acid. Although the chemical property o insolubility is the essential one that recommends vitreous silica for this use, the physical property of small thermal expansion is almost equally

important, for it nearly eliminates the danger of breakage which was always present with glass stills.

Vitreous silica serves the laboratory as well as the works, on account of its insolubility in pure water or in acid solutions. It is attacked only by hydrofluoric and concentrated phosphoric acids. The purest "conductivity water" is made by distillation in vitreous silica.

(D) Uses depending upon absorbing power

Practically all solids carry a tightly adhering film of atmospheric substances (O, N, H_2O, CO_2) together with odds and ends of other substances picked up during their history. Although usually almost unweighable, these sorbed substances become relatively large in amount when the exposed surface per unit weight becomes very large, or when sharp re-entrants in the surface cause substances which are relatively dilute in the surrounding medium to be condensed or concentrated in the surface.

The micro-amorphous variety of silica called diatomite has these surface qualities, and has long been used as a filtering medium for impure oils, sirups, and other liquids.

In imitation of the natural product, the micro-amorphous variety known by the trade name of "silica gel" has been patented and manufactured in recent years. In addition to acting as a filtering agent for oils, etc., it very efficiently absorbs water out of a mixture of less condensable gases and in general will fractionate a gas mixture by differential absorption. It is not yet competing on a large scale with natural silica but has important possibilities.

(E) Use as a source of silicon

The alloys known as "ferrosilicon" are now widely used in the manufacture of iron and steel. Silicon serves as a deoxidizer of the molten metal, and also imparts special properties if added in sufficient amount to make a "silicon steel". Ferrosilicon alloys containing from 8 up to 95 per cent silicon are made by the reduction of iron ore and silica in the blast furnace or the electric furnace. Low-percentage ferrosilicon can be made from siliceous iron ore, but the higher percentages are made with quartz sand or crushed quartz as raw material. Freedom from phosphorus, arsenic, and sulfur are important qualities for this use.

Quartz sand also serves as raw material for the manufacture of silicon carbide (SiC) in the electric furnace.

Chapter XLVII. PHYSICAL USES OF SILICA

As defined in Chapter XLIII, a "physical use" is one in which the substance maintains its individuality, and in which it can be replaced by any other substance having the desired primary property. The physical uses may therefore be classified in the same way as the properties described in Chapters III to XL. Making slight changes in the order, we have the following outline:

A. Uses depending on volume
B. Uses depending on mechanical properties
C. Uses depending on thermal properties
D. Uses depending on electrical properties
E. Uses depending on radiational properties

The use of silica as a refractory, depending upon its high melting-point (Chapter VI) has already been considered in a separate chapter (XLV).

(A) Volume

The use which consumes by far the largest tonnage of silica is one depending mainly on the fact that it occupies space, namely, its use as gravel and sand in cement-concrete and in mortar. Mechanical strength is an important supplementary property, but is not the essential one, as shown by the fact that coke and granular calcite have been used for the same purpose.

Another very different use which belongs in this class is the use of finely ground quartz or of chalcedonic silica as a filler. The fine-grained white silica of southern Illinois, for example, is used as a wood filler; as a "reinforcer" in zinc and lead paints; and as an inert material in mixed paints and varnishes, to replace whiting or barytes.

Allied to the above is the use of diatomite as an absorbent, or rather a sustainer, of liquids, such as nitroglycerin in the manufacture of Nobel's original type of dynamite.

(B) Mechanical properties

These uses arise principally from the mechanical strength and the hardness, especially abrasion-hardness, of quartz. The elastic properties and the flowage of vitreous silica must also be considered here.

Mechanical strength of the quartz grains and of the siliceous cement leads to the use of sandstone for the construction of foundations, walls,

bridges, etc. Quartzite is less used for such purposes because of the difficulty of shaping it.

Two groups of uses depend on hardness: (a) use as a crushing agent, and (b) use as an abrasive agent,

(a) *Crushing agent*

Flint pebbles (p. 803) represent the greatest tonnage as a crushing agent. They are employed in ball mills and tube mills for grinding a great variety of materials. Their principal source has been the nodule-bearing chalk beds of England and France.

Stone mortars, and the familiar agate mortars of the laboratory, form another example of this use; likewise the sandstone and quartzite mill-stones and buhrstones, used for crushing and milling cereals, paints, fertilizers, etc.

(b) *Abrasive agent*

Silica is used as an abrasive in the form of sandstone, quartz sand, crushed quartz, chalcedonic silica, and diatomite.

Sandstone of certain grades is used for making grindstones and pulp-stones. The principal center for this industry in the United States is in northern Ohio where the "Berea grit" is quarried and cut. Small sharpening stones, whetstones, and hones are made of finer grained material such as the novaculite of Arkansas (Tab. XLII.6). Artificial abrasives such as carborundum have cut into this industry somewhat in recent years, but the silica stones are still preferred for many purposes.

Loose quartz sand is used as an abrasive in the cutting of stone by means of metal saws, and in sand-blasting. The sand-blast has been adapted to a great variety of purposes, such as cleaning stone buildings, cleaning surfaces of metal, cutting designs on glass, etc.

In a fixed, rather than loose, form, quartz sand and crushed quartz are used on sand-paper and sand-belts.

For scouring and polishing, a very fine-grained abrasive is needed, and one which can be guaranteed free from particles which are noticeably coarser than the average. Finely divided crystalline silica such as that of southern Illinois is much used in scouring-soaps and in polishes for metal; also as a substitute for pumice in finishing metal and wood. Diatomite has been applied to scouring and polishing since early times, being often given the name "tripoli" or "tripoli powder" because much of it came from beds near Oran in Tripoli, northern Africa.

Under this general classification of uses depending upon hardness and abrasion should be placed one use of quartz sand which ranks quite high in tonnage, about equal to glass sand and outranked only by building sand and molding sand. I refer to its use as "engine sand", which is poured in small amounts on the steel rails of a track in order to prevent slipping

of the wheels of a steam locomotive or electric motor. About two million tons were used for this purpose in the United States in 1924.

One could cogitate all day without thinking of the following odd abrasive uses for fine-grained silica, but they consumed enough of the product from southern Illinois to be worth reporting: billiard-cue chalks and chicken grits.

Quartz weights

The high abrasive-hardness of quartz cooperated with its chemical inertness to suggest long ago that it would be an excellent material for standards of mass. The constancy of quartz weights is shown, for example, by some comparisons of Austrian 500-mg standards made by Seidel.[2] The difference between two quartz standards was 3.45 mg in 1846-7, and was 3.43 mg in 1867, a difference of only 0.02 mg in 500 000 mg after 20 years. Several national standards have been made of quartz (see p. 293) but the preference at present seems to be for metallic weights. It may fairly be questioned whether a uni-crystalline material like quartz is not likely to be more constant in its properties than an aggregate such as a cast metal or alloy.

Applications of the elastic properties of vitreous silica

The elastic constants of vitreous silica and its phenomena of delayed elasticity and flow have been discussed in detail in XXIII and XXIV. The very small magnitude of the elastic after-effects has made silica fibers very valuable in the laboratory, as suspensions for delicate rotational or deflectional apparatus, and they have been without a rival where a non-conducting fiber is desired for such purposes.

The method usually used for making vitreous silica fibers is the bow-and-arrow method originally devised by Boys.[3] By this method silica fibers can be made of any size down to a diameter too small to be seen under a high-powered microscope. Such a fiber vanishes into diffraction bands whose motion shows that a fiber is still present though invisible. Its diameter is less than 0.25 μ, or less than about 500 atom-triplets of SiO_2. The smallest one which has been made and handled is estimated at 25 mμ or about 50 atom-triplets.

Dufour's method[4] of making a fine thread of silica was to draw it rapidly from the molten fragment on to a rotating spool. This does not make as fine a thread as the cross-bow method of Boys, the minimum by Dufour's method being about 10 μ.

The small elastic after-effects also suggest the use of vitreous silica for tuning-forks, since the decrement should be small (p. 452) and there

[2] Steinheil, C. A., Denkschr. Kais. Akad. Wiss. Wien, Math.-Nat. Cl. (1867) 27 I: p. 183.
[3] Article cited in XXIII, note [28].
[4] Article cited in XLIV, note [10].

would be little change of pitch due to change of period with decreasing amplitude. Again, metal forks change with temperature, because of their large thermal expansion, and this change would be eliminated in vitreous silica. The effect of temperature is not only on dimensions, however, but also on the elastic constants, and in this respect the temperature effect in vitreous silica would not be negligible.

Vitreous silica thermometers

One of the most troublesome features of a mercury-in-glass thermometer when used at high temperatures is the change of zero resulting from flow. This effect is almost completely absent from vitreous silica at a temperature where a thermometer-glass shows considerable distortion. Shenstone accordingly predicted the early use of vitreous silica for such thermometers, but developments in this direction were slow. Its possible usefulness in fundamental gas thermometry was quickly realized, and bulbs of it were tried out, but their permeability to hydrogen and helium has somewhat discouraged this use.

The greatest difficulty with metal-in-glass thermometers made of silica has been to make a capillary of sufficiently uniform bore. Dufour made a vitreous silica thermometer containing tin as the expanding liquid, and also one with mercury, but the art was not followed up in France, so far as I am aware. At present, mercury thermometers reading to about 750°C are obtainable from Siebert & Kühn, who have cooperated with Heraeus in Germany. Some gallium-filled thermometers graduated to 1000° have been made recently by the General Electric Company [5] but are not commercially available. Whether the zero will be sufficiently constant at so high a temperature may be doubted (see p. 475).

(C) Thermal properties

Thermal dilatation

The small thermal dilatation of vitreous silica suggests a number of uses, one of which has already been commented upon (p. 824).

One very important result of the low thermal dilatation combined with high mechanical strength is the resistance of vitreous silica to sudden heating and cooling. Perhaps its use in acid-manufacturing works should be ascribed to this property as the primary one rather than to its insolubility, because even at a high price it will replace any ordinary glass, insoluble though it be, on account of the diminished breakage.

This property recommends it also for lamp globes for gas lighting, especially out of doors or in exposed places, a use which is coming to be an important one in England. In the United States gas is so little used for lighting that the demand for silica globes is not likely to be important.

[5] Boyer, S., Ind. Eng. Chem. (1925) 17: 1252-1253; J. Opt. Soc. Amer. (1926) 117-122.

Standards of length

Its very small dilatation combines with its favorable mechanical qualities to make vitreous silica a material worth studying as regards its suitability for standards of length. Being a glass, however, it is subject to suspicion because of the well-known changes of dimensions that occur in the complex silicate glasses. It must first be shown that a vitreous silica rod remains satisfactorily constant in length over many years.

The vitreous silica standard meter of the National Physical Laboratory, as described by Kaye,[6] consists of a silica tube into which are fused, at the ends, optically plane parallel slabs of the same material. These slabs carry the graduations defining the meter length. The under side of each slab was first platinized, and the graduations were then made by cutting through the platinum with a diamond point; this method yields sharper and cleaner lines than can be ruled on a polished metal surface. The length is read with the tube immersed in water and supported at the "Airy points" by means of vitreous silica trunnions sealed to the tube.

In spite of the smallness of the dilatation of vitreous silica, quartz may prove to be a more promising material for length standards, except for the fact that it is not obtainable in lengths such as a meter. The International Bureau of Weights and Measures at Paris has had prepared length standards in the form of plates and prisms, of dimensions 1, 2, 4, 6, 8, 10, 20, 30, 40, 50, and 100 mm. The lengths have been measured by Michelson's interferometric method in terms of four standard wave-lengths, and future measurements will indicate their dependability as standards as well as the experimental reproducibility of the wave-lengths used. In view of facts presented in XXVIII, XXXIII, and elsewhere in this book, some experiments on the immediate, rather than long-term, effects of atmospheric humidity and of accidental electrification might be instructive.

Thermal conductivity

The very small thermal conductivity of diatomite has led to the use of large quantities of the product from southern California as a heat insulator, in ovens, refrigerators, walls of buildings, etc. This use can hardly be accredited solely to the properties of the constituent substance silica, but rather to the properties of the aggregate as a whole. Almost any non-metallic aggregate having the finely porous structure of diatomite would have a similarly low thermal conductivity.

(D) Electrical properties

The principal uses to be commented upon in this group are: (a) use as an insulator, (b) use as a constituent of piezo-electric apparatus.

[6] Article cited in XXIV, note [25].
[7] Pérard, A., article cited in XXXI, note [24].

Vitreous silica is one of the best insulators known. Its resistance is practically not affected by atmospheric humidity, and it is the only good insulator which is not damaged by heating to a red heat.

Kaye[8] says of it: "Unfortunately the modern furnace methods of production cannot be relied upon to yield a product which possesses the insulating properties of the more expensive silica made by the oxy-hydrogen flame. This remark applies alike to the clear transparent variety and the air-streaked satin-like kind".

The supposed differences in insulating power due to method of manufacture could not be substantiated by Curtis.[9] He found that a piece of old silica tubing made by Heraeus in 1904 gave the same results, when cleaned in the same way, as the cleaned vitreous silica whose curve of surface resistance has been shown in Figure XXVII.8. Another specimen "of inferior manufacture", not specially cleaned, agreed with the lower curve in this same Figure. The specimens are all alike in resistivity so far as these experiments show.

Applications of the piezo-electric property

The piezo-electric phenomena in quartz were applied by J. & P. Curie[10] to the measurement of electric potentials up to several thousand volts. Two very thin rectangular plates of quartz are cut perpendicular to the electric axis, with the longer direction of the rectangle perpendicular to both the electric and the optic axis. One plate is turned around 180° on the other, and the two are cemented together. When a difference of potential is applied, one plate expands and the other contracts and the pair bends: if one end of the pair is fixed, the free end moves and gives a measure of the potential difference.

A piezo-electric plate (see Fig. XXVIII.4) is also a very sensitive quantitative source of electric charges. A plate of about the dimensions 60 × 15 × 0.5 mm can support conveniently a weight of 5 kg. This can supply about 60 e. s. u. of electricity, and with an electrometer of ordinary sensitiveness (5 mm deviation per volt at 1 m) makes possible the measurement of currents over the range 10^{-9} to 10^{-13} ampere.[11]

A new use for the piezo-electric phenomenon in quartz is its application by Karcher[12] to the measurement of nearly instantaneous high pressures. The electric charge liberated when pressure is applied passes through a galvanometer of long period and small damping, whose deflection is recorded photographically on a rapidly moving film.

The method can be applied to such diverse problems as the firing of

[8] KAYE, G. W. C., *X-rays* (1923, London).
[9] CURTIS, H. L., article cited in XXVII. note [21].
[10] Compt. rend. Acad. Paris (1888) 106: 1287-1289.
[11] CURIE, MME. P., *Traité de radioactivité* (1910, Paris) 1: p. 95.
[12] KARCHER, J. C., Sci. Pap. Bur. Standards (1922) 18: 257-264 (No. 445).

a heavy gun, or the "force of the blow" struck by a hammer, a rifle bullet, a boxer's fist, or a watch escapement.

For use in a heavy gun the piezometer consists of a stack of quartz plates mounted in a steel container in the form of a plug which is screwed into the breech-block. The pressure is applied to the quartz through a piston, since the pressure must be unidirectional, not uniform. In one form of gage, as used by Karcher, six plane-parallel plates of quartz, cut perpendicular to an electric axis, are mounted with thin sheets of platinum between them, the plates being arranged so that faces of the same polarity are in contact with a given sheet of platinum. Positive and negative leads are then brought out from alternate sheets to the galvanometer. The use of a stack of plates serves to increase the total charge-yielding area.

It can be shown that with a long-period, slightly damped galvanometer the angular speed of deflection of the galvanometer coil is proportional to the pressure. The photographic record gives the curve of angle against time. The differential of this curve, multiplied by an experimentally determined constant, therefore yields the curve of pressure against time

$$\Phi = f(Z), \text{ and } p = \frac{d\Phi}{dZ} = \frac{df(Z)}{dZ}$$

The piezo-electric method of pressure measurement has the great advantage that there is practically no movement of the piston, and the troublesome effects of inertia and friction are thus eliminated.

Another recent use of the piezo-electric property, now rapidly increasing in importance, was devised by Cady,[13] namely, its use for stabilizing the frequency of amplifier tube circuits. A plate of quartz placed loosely between electrodes to which is applied an alternating voltage, having a frequency near the natural mechanical vibration-frequency of the plate may act as a "feed-back" or may be made to supply piezo-electric alternating charges through an additional pair of electrodes, thereby maintaining the frequency constant to 1 in 10 000 or better. (See also pp. 567 and 805.)

(E) Radiational properties

The radiational properties which are most important in recommending silica for this class of uses are: (a) transparency to visible light, (b) transparency to the ultra-violet, (c) rotatory power.

(a) *Visible transparency*

Its high degree of transparency, and its freedom from the interfering flaws which are found in any glass excepting the modern types of optical glass, joined with its hardness and the resistance of its surface to weathering, have always made rock crystal a much prized material for decorative objects. In the days when everyone had plenty of time, some wonderful

[13] Cady, W. G., Proc. Inst. Radio Eng. (1922) **10**: 83-114.

fine vases and similar objects were painfully worked out by hand from transparent quartz. At present, the most highly valued articles of this kind are the crystal spheres, many of which come from Japan.

Some of the applications of crystallographic facts to the working of quartz are of interest. The Japanese workers in quartz very early learned to take advantage of such faintly distinguishable cleavage,—or effects of gliding planes resembling cleavage,—as is shown by the crystalline substance (see p. 488). A sculptor at Kofu is said to have discovered the fact that a crystal can be cleaved parallel to the trigonal prism by first making a shallow groove perpendicular to the oscillatory combination of prismatic and rhombohedral faces found on some crystals, and then striking this groove with a wedge.

The fact that fracture perpendicular to the axis is more regularly conchoidal than in other directions is also taken advantage of in blocking out spheres or sculptured forms. With a small hammer and narrow steel chisel the superfluous quartz is chipped away by a succession of conchoidal fractures all perpendicular to the axis. Excess material is also removed, for complicated forms, by means of a steel wire and emery.

The smaller hardness in the basal plane is likewise taken advantage of. Quartz seals are so oriented that the letters can be cut in a basal plane. The vertical hole for a hollow sphere or a vase is drilled parallel to the axis.

I once saw in the hands of a lapidary a partly completed pocket-watch which was being made for a wealthy broker who had a fancy for oddities, and which was to be made entirely of transparent quartz with the exception of the mainspring and hairspring. I trust that the lapidary was enough of a crystallographer to cut all his wheels perpendicular to the optic axis, else some surprising effects must have resulted when the circular wheels became elliptical with changing temperature (see p. 367).

Spectacle lenses.—In spite of the modern introduction of various kinds of glass made in an optical quality sufficiently good for spectacle lenses, there is still a demand for such lenses of quartz, and their manufacture is a continuing though perhaps not a growing industry. When Brazilian quartz pebbles first began to appear in English and European markets, the demand for them came almost entirely from the spectacle manufacturers.

(b) *Transparency to ultra-violet*

The transparency of optical systems containing silicate glasses extends in general only to about 340 mμ, very little beyond the visible, and this sets a limit to the usefulness of such apparatus for a number of different purposes. When it was discovered that quartz is transparent in the ultraviolet region out to a wave-length of 185 mμ, the field of spectroscopic research was practically doubled, since the limit was thereby placed as far above the visible violet as the violet is above the red. The production of isotropic vitreous silica, with a similar transparency, was in some respects

a still further advance, although its transparency to ultra-violet is somewhat less than that of quartz (p. 719).

It is this transparency to the near and middle ultra-violet that has brought vitreous silica into one of its principal uses, namely, as a material for electrical discharge tubes which are to serve as a source of ultra-violet radiation. The most commonly used source is the "mercury arc". The electric discharge through mercury vapor yields many emission lines in the ultra-violet, and the discharge is easy to start and maintain.

The mercury arc can be produced in tubes of ordinary glass and a part of the ultra-violet can be obtained, but nearly all of the wave-lengths smaller than 340 mμ are absorbed by the glass. These wave-lengths may be allowed to escape by the use of windows of quartz or of vitreous silica, but such windows cannot be sealed directly to soft glass and must therefore be cemented in place. Such cemented joints are likely to crack or leak and the window device is therefore less satisfactory than a lamp made entirely of silica. The all-silica lamp also permits the use of a much greater intensity of current and hence a more intense radiation, because it will withstand a higher temperature than ordinary glass.

Many forms of the vitreous-silica-mercury arc lamp have been devised and used, and there are numerous patents on improvements in construction and operation and on the addition of other metals to the mercury.[14]

Other metals which have been used in vitreous silica as sources of ultra-violet radiation are cadmium, sodium, and potassium. Gas discharge tubes, also, containing helium, neon, etc., have been made of silica with resulting elimination of some of the difficulties due to the escape of gases and water from soft glass.

For obtaining a continuous spectrum in the ultra-violet, above 200 mμ a tungsten incandescent filament in a vitreous silica bulb, or a tungsten lamp with a quartz window, has been used.

Ordinary glass cuts off much of the Sun's ultra-violet radiation, and the use of vitreous silica windows in such places as hospital solariums is being seriously recommended.

The numerous chemical and medicinal uses of ultra-violet radiation need not be gone into here.

The transparency of crystalline quartz to the near and middle ultra-violet makes it very useful in the study of spectra of chemical elements and compounds. The quartz spectrograph has made possible the easy photographing of many lines inaccessible to an apparatus containing optical parts made of the usual complex soft glasses.

(c) *Rotatory power*

The dispersion of the rotatory power of quartz and that of solutions of cane sugar are nearly the same. This fact led to the invention by Soleil

[14] Much of the literature on these subjects is summarized or abstracted in a recent book by Luckiesh, M., *Ultraviolet radiation* (1922, New York).

of the saccharimeter. In this instrument the rotatory power of quartz is used to compensate the rotatory power of the solution, and white light, with its relatively great intensity and its practical convenience, can be used because all the frequencies are compensated very nearly together. The polarizer and analyzer are fixed in the crossed position, and the rotation due to the column of sugar solution placed between them is compensated by introducing a variable thickness of quartz, obtained by sliding one or more wedges of the crystal across the field.

For calibrating such instruments, standard quartz plates, whose rotation is equivalent to that of the conventional sugar solution, are employed. The quartz for such plates and also for the wedges must be of the highest quality.

The commonest and most troublesome defect in quartz intended for optical work, including polarimetry and saccharimetry, is the occurrence of twinning (see XII). The axes of two neighboring independent units which are in twinning relation are likely to be not quite parallel. The resulting birefringent effects may spoil the specimen for optical uses.

The old standard test for this defect is made with the "Nörrenberg polarization apparatus." Skylight is reflected downward from a glass plate upon a horizontal mirror, and returns from the mirror up through the glass plate into an analyzing Nicol prism, then to the observer's eye. The light is partially polarized by its first reflection, and the analyzer can be set to a position of darkness. If a plate of quartz cut exactly perpendicular to its optic axis is placed on the mirror, it will have no effect on the light if it is homogeneous, but if it is twinned and there are slight angles between the axes of the twinned units, parts of the crystal will appear to light up and become colored. Such specimens are called "bunte" by the German instrument maker.

A more sensitive test than the Nörrenberg is the "Schlieren-methode" or method of striae,[15] a method often used for studying imperfections in lenses and photographing waves in gases and liquids. It depends upon minute variations in refractive index, and might therefore fail to reveal an intergrowth of dextro- and levo-quartz if the index happened to be very constant. It does, however, reveal certain inhomogeneities whose cause is not clear, but which may be due to uneven distribution of some impurity.

Brodhun & Schönrock[16] recommend as most sensitive a method of compensation, wherein the rotatory power of the plate to be tested is compensated with quartz wedges in a specially arranged polariscope.[17]

With the increasing use of saccharimeters in industry came an increasing demand for standard quartz plates, with the result which so often follows upon attempts to increase the supply and lower the price at the same time, namely, a lowering of the quality. Complaints began to come to the national testing bureaus that the standard quartz plates did not agree, and the blame was laid by some users on a supposed variability in

[15] Töpler, Ann. Phys. u. Chem. (Pogg.) 1866 to 1868.
[16] Brodhun, E., & Schönrock, O., Zeitschr. Instrum. (1902) **22**: 353-372.
[17] See also Williams & Twyman, Glazebrook's *Dict. applied physics* (1923) **4**: 661.

the rotatory power of the quartz itself according to the source from which it came.

Gumlich[18] showed that this suspicion was quite unfounded, and that the rotatory power of reasonably well selected quartz is constant to an extent well in excess of industrial requirements. This judgment has been confirmed by later investigations. Gumlich found that the usual defect which was responsible for the complaints of lack of constancy was a lack of parallelism in the faces of the plates, and therefore to be laid at the door of the optician rather than blamed on Nature. (See also p. 650).

Aside from the quality of the material itself, the principal defects in quartz plates intended as polarimetric standards are (1) lack of planeness and parallelism of the faces, resulting in variable thickness; (2) deviation of the face of the plate from exact perpendicularity to the optic axis. Sensitive methods of testing for these defects have been described by Gumlich, Brodhun & Schönrock, and others.

Thermometric use of rotatory power.—Joubert[19] recommended the rotatory power of quartz as a convenient and very sensitive thermometric property. He himself used as a thermometer in some of his researches a piece 8 mm in diameter and 15 mm long, set in a shell of copper to avoid too rapid or irregular heating. Such a thermometer would be quite practicable, and could be made very sensitive, for temperatures up to 550°. At higher temperatures there would be too much danger of breakage at the inversion-point.

Use in colorimetry.—The color effects obtainable from white light because of the dispersion of the rotatory power of quartz have been applied by Priest[20] in the construction of one of the most satisfactory colorimeters yet devised, since it is independent of arbitrarily selected color standards and rests only upon precise quantitative measurements of a property of a reproducible substance.

[18] Article cited in XXXIII, note [6].
[19] Article cited in XXXIV, note [34].
[20] PRIEST, I. G., J. Opt. Soc. Amer. (1923) 7: 1175-1209.

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